PELICAN BOOKS

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EXPLOSIVES

Tells of Explosives, their Magical Creation, their Fierce Energy, their Sudden Disruption, their History and Romance, and their Uses in Peace and War

JOHN READ

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EXPLOSIVES

BY

JOHN READ

Most of us regard explosives merely as agents of destruction, and we have little knowledge of their sources and of the factors that determine their spectacular activity. Nor do we realise that the story of explosives is one of great diversity and fascination, in which peace and war, science and industry, history and romance, human intellect and personality all have a part.

This story has remained untold in a coherent form because it is bound up with details which have been viewed as a preserve of the specialist, and in particular of the chemist. Dr. Read has specialised in chemistry and also in taking broad views of chemistry and its manifold associations, which he has expounded to all sorts and conditions of men, ranging from Australian miners and bushwhackers to school-children, university students, and members of learned societies.

The stage is a vast one, and the spotlight moves from the mediaeval cell of Roger Bacon to modern munitions factories, and dwells in turn upon the world's sources of energy and the three main pillars of the explosives industry—fats, cotton and coal. Dyes, drugs, petroleum, fertilisers, soap, and many other familiar commodities also form part of the mosaic of a narrative which will rank as a picturesque addition to the literature of science.

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PELICAN BOOKS

EXPLOSIVES

BY

JOHN READ

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TO A FUTURE ENLIGHTENED AGE WHICH SHALL SEE "THE MARVELLOUS POWER OF ART AND NATURE", AS FORESHADOWED BY ROGER BACON, RANGED WHOLLY ON THE SIDE OF HUMANITY

MRS. B.

If you are not yet tired of experiments, I have another to show you. It consists in filling soap-bubbles with a mixture of hydrogen and oxygen gases, in the proportions that form water; and afterwards setting fire to them.

CAROLINE.

Here is a fine large bubble rising—shall I set fire to it with the candle?

MRS. B.

If you please . . . .

CAROLINE.

Heavens,* what an explosion!—It was like the report of a gun: I confess it frightened me much. I never should have imagined it could be so loud.

EMILY.

And the flash was as vivid as lightning.

MRS. B.

The combination of the two gases takes place during that instant of time that you see the flash, and hear the detonation.

MRS. JANE MARCET,

Conversations on Chemistry, 5th ed., 1817.

* This ejaculation, being considered unsuitable for young ladies in 1817, was removed from later editions.

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ABBREVIATIONS, WEIGHTS AND MEASURES

The following abbreviations, recognised generally for scientific purposes, are used in this book. Some relationships between the Metric and British Imperial weights and measures are added, the former system being used almost exclusively in scientific work.

B.p. boiling-point (°C.)

C. Centigrade. All temperatures in the text refer to this scale. To convert to the Fahrenheit scale, multiply by 9/5 and add 32: for example, 65°C. = 149°F.

c.c. cubic centimetre (1000 c.c. = 1 litre = 1·76 pints = 0·22 gallon).

cm. centimetre (2·54 cm. = 1 inch; 100 cm. = 1 metre = 39·37 inches).

g. gram (1 g. = 15·432 grains; 28·35 g. = 1 oz.)

g.-cal. gram-calorie (see p. 20).

kg. kilogram (1 kg. = 1000 g. = 2·20 lb.)

kg.-cal. kilogram-calorie (see p. 20).

m.p. melting-point (°C.)

CHAPTER I

A FIRST ANALYSIS

"THE word politics, sir," said Mr. Pickwick, "comprises, in itself, a difficult study of no inconsiderable magnitude." If we substitute "explosives" for "politics"—and the two subjects are not entirely dissimilar—these are "fine words to begin a chapter," as Count Smorltork remarked of the original dictum.

At first sight, the story of explosives may appear as a very circumscribed subject, with little interest beyond its connection with the activities of warfare, rather than as "a difficult study of no inconsiderable magnitude." From the beginning, however, it must be emphasised that even a purely technical survey of the subject discloses the fact, at once illuminating and encouraging, that in times of peace the output of explosives, although very large, is devoted chiefly to civil purposes. Against the destructive abuses of explosives in war must be set their constructive uses in peace: these uses, as the sequel will show, are surprisingly great. Modern civilisation, indeed, owes a great deal to the rightful application of explosives. Economic, political, and even geographical considerations of primary importance are clearly bound up with such impressive undertakings as the construction of the Panama Canal, which would have been impracticable without the aid of the powerful explosives elaborated in modern times.

The present treatment is not limited to a purely technical survey of the subject. In common with other branches of science, this particular field of man's practical and intellectual endeavour has a strong historic appeal, tinged here and there with romance. Across the pages that follow, flit such intriguing figures as Roger Bacon, "the greatest apparition of the Middle Ages"; Berthold Schwarz, or Black Berthold, the mysterious monk of the Black Forest; Dr. John Clayton, the Yorkshire rector whose interests ranged from "Observables in Virginia" to an inflammable Spirit of Coal; Scheele, the struggling Swedish apothecary; his fellow

countryman, Nobel, rich beyond the dreams of avarice; Chevreul, the centenarian French chemist; and Alexander Forsyth, the ingenious Highland minister and ardent fowler.

It may be claimed further that the romantic appeal of the subject has a chemical side little less interesting than the humanistic: for the immediate actors in this dramatic story are the explosives themselves, together with the atmospheric gases whence they are slowly woven by magical creation and unto which they return in the twinkling of an eye—shedding suddenly, like the Djinn of an Eastern tale, their fabulous stores of strangely acquired energy. It is an arresting reflection that fierce explosives like nitro-glycerine, guncotton, and trinitrotoluene are evolved from the harmless atmospheric gases, carbon dioxide, nitrogen, and oxygen, by the operation of synthetic processes, partly natural, partly artificial, leading to new and complex molecular patterns and vivified by the radiant energy of the sun.

In a broadly conceived account of the story of explosives, each of these diverse aspects of the subject must be elucidated. A little reflection will show that even the simplest scientific treatment must be founded on a chemical basis. Accordingly, since the present book is a self-contained unit starting from first principles, the account opens with a chapter in which the underlying chemistry is explained in as brief and simple a manner as seemed possible. To the reader who has passed through an ordinary school course of chemistry this chapter should present little difficulty; the newcomer to physical science must decide according to his aims and interests whether it is to be tasted, swallowed, or chewed and digested.

As Elias Ashmole observed of astrology, in 1652, there are in chemistry "(I confesse) shallow *Brookes*, through which young *Tyroes* may *wade*; but withall, there are deepe *Foards*, over which even the *Gyants* themselves must *swim*." Even the tenderest tyro, provided he be interested and resolute, should find it possible to wade without discomfort through the chemical chapter to the more solid shores that lie beyond.

CHAPTER II

WHAT IS CHEMISTRY?

Civilisation's Chemical Milestones

CHEMISTRY is a branch of science which deals with the composition of materials of all kinds. Primitive man took his materials as he found them ready at hand in Nature, and it was only gradually that he began to gain control over them and adapt them to his uses. To a chemist it is significant that archæologists have recognised three main stages in the gradual evolution of civilisation under the names of the Stone Age, the Bronze Age, and the Iron Age. Man's pilgrimage along the highway of history is marked in this way by chemical milestones. Perhaps the fourth milestone will be known as the Petroleum Age, or, in wider terms, the Age of Organic Energy.

It has been a long journey from fig leaves to viscose silk and nylon, from the wood fire to high-tension electricity and the internal combustion engine, from primitive charms to aspirin and synthetic vitamins, from the sling to the magazine rifle and the fourteen-inch gun. As man has made his way along this never-ending road he has learnt slowly and painfully to discriminate between various kinds of matter, to separate them from each other, and to gain some knowledge of their properties, uses and composition. In short, with his mounting mastery over materials he has grown more and more chemistry-conscious. This does not mean that the average educated man of the twentieth century is yet conscious of a knowledge of chemistry. Empirically, however, he has a casual acquaintance with the application of a vast range of recognised chemical facts that would have astounded and delighted great scientists of the past, like Boyle and Newton. It is the purpose of the present chapter to build upon this foundation.

Substances and Chemical Change

The "stuff" of the material universe is of mixed composition, but it may be separated into individual ingredients known as **substances**. Chemistry is concerned with such separative processes. It deals with the composition of each distinct substance. It takes

account also of the utilisation of substances, in either analytical (breaking-down) or synthetical (building-up) processes, for the production of other substances. Separation, composition, and transformation are three of the most important words in the chemist's vocabulary; his science is dynamic (moving) rather than static (still), and he is particularly interested in changes of composition.

When a substance undergoes a purely physical change its composition remains unaltered. When a substance undergoes a **chemical change** a new substance of different composition is invariably formed. The same substance, however obtained, always has precisely the same composition.

Sea-water is a common material which may be quoted in illustration. Being a mechanical mixture, and not a single substance, its composition is found to vary, depending upon its precise source. When submitted to the physical process of distillation it yields distilled water and residual sea-salt, without undergoing any chemical change. Distilled water is a chemically distinct portion of the original mixture, and is thus a single ubstance. Sea-salt is a mixture of solid substances; but by the hysical process of crystallisation it may be separated into its onstituent substances, such as sodium chloride (table salt) and magnesium chloride.

When pure water is frozen it changes from a liquid to a solid, and when it is boiled it passes into a vapour or gas. These are physical changes, because ice, water, and steam all have the same chemical composition. When steam is raised to a very high temperature, however, it yields two colourless gases, oxygen and hydrogen; a similar result is reached when acidulated water is electrolysed. These are chemical changes, because they bring about a change of chemical composition, leading to the formation of other substances. Similarly, sodium chloride undergoes a chemical change when it is heated with sulphuric acid, since in conjunction with the acid it yields two fresh substances, sodium sulphate and hydrogen chloride. Again, when sodium chloride is fused and electrolysed it undergoes another chemical change, resulting in the formation of two other substances, sodium and chlorine. Such processes are examples of **chemical reactions**.

Elements and Compounds

Substances may be classified as **elements** or **compounds**. Compounds, unlike elements, can be broken down into simpler substances. Water can be broken down into hydrogen and oxygen, and sodium chloride into sodium and chlorine: thus, water and sodium chloride are compounds. Hydrogen, oxygen, sodium and chlorine are elements, because they cannot be broken down into simpler substances. Altogether, about ninety different elements are known, and these form the building stones of a vast number of compounds.

It is a point of fundamental importance in chemistry that the properties of a compound cannot be predicted from those of its constituent elements. The properties of a compound are not the sum of the properties of the elements from which it is formed. To take a simple example, the two elements sodium and chlorine combine readily to form a compound called sodium chloride. Sodium is a soft, silvery-white metal which reacts vigorously with cold water to form an intensely caustic solution ("caustic soda"). Chlorine is a poisonous and suffocating gas. The sole result of their combination is a substance that may be sprinkled with confidence and beneficial results upon a bowl of porridge: this substance is commonly known as table salt.

Molecules and Atoms

Matter is said to have a discontinuous or grained structure. This conception underlies the **Atomic Theory** of John Dalton (1808). The "grains"—known as **molecules**—are so excessively minute that the most powerful microscope fails to disclose their individual existence. Indeed, according to Lord Kelvin, if a drop of water could be magnified to the size of the earth its constituent molecules would fall into a range of magnitude bounded on one side by small shot and on the other by cricket balls. These tiny entities, however, possess a structure of their own, their constituent parts being known as **atoms**. Thus, the ultimate chemical particle —or molecule—of water is composed of two atoms of hydrogen and one atom of oxygen. These three atoms are held together within the molecule by the force of chemical affinity. A speck of

water magnified on Lord Kelvin's scale might be compared in a rough and ready way to a mountain of walnuts. Each walnut represents a molecule: the two halves of the shell represent two hydrogen atoms, and the kernel represents an oxygen atom. A chemical change cracks the walnuts; a physical change does not. In more scientific phraseology, a chemical change alters the structure of the molecule; a physical change does not.

All the molecules of a particular substance are alike. The molecules of elements contain only one kind of atom, but those of compounds contain more than one kind of atom. For example, the hydrogen molecule is composed of two hydrogen atoms (the two halves of the walnut shell); but the water molecule contains two hydrogen atoms and one oxygen atom (the two halves of the walnut shell and the kernel).

Each atom has its characteristic weight. As this weight is excessively minute, it is customary to assign unit weight to the lightest of all known atoms—that of hydrogen—and to refer all other atoms to this standard. Thus, the statement that the **atomic weight** of oxygen is 16 means that the oxygen atom is sixteen times as heavy as the hydrogen atom. From this it follows that the **molecular weight** of water is the sum of the atomic weights of its constituent atoms, that is, 16 + 1 + 1, or 18; or, in other words, a molecule of water weighs eighteen times as much as an atom of hydrogen. It is now evident that a knowledge of the **molecular composition** of a substance enables one to calculate its percentage composition. For example, 2/18ths of a water molecule is composed of hydrogen and 16/18ths of oxygen; so that the water molecule—and therefore water in bulk—contains 11·1 per cent. of hydrogen and 88·9 per cent. of oxygen by weight.

Returning to our walnuts as models of water molecules, we may assign the standard weight of 1 unit to each half of the shell. The kernel then weighs 16 units, and the complete walnut weighs 18 units. Thus, 2/18ths of a walnut (water molecule) is composed of shell (hydrogen) and 16/18ths of kernel (oxygen). Each walnut therefore consists of 1/9th of shell and 8/9ths of kernel, by weight. Consequently the whole mountain of walnuts, or walnuts in bulk, contains 1/9th (11·1 per cent.) of shell and 8/9ths (88·9 per cent.) of kernel. The composition of the mountain

is the same as that of each individual walnut, since these are all alike. This is true both for the *qualitative* composition (which concerns the *kinds* of constituents—shell and kernel) and the *quantitative* composition (which concerns the *quantity* or proportion of each constituent). From such considerations it is seen that all the molecules of any specific substance are alike, both qualitatively and quantitatively; further, that the same substance, however obtained or prepared, always contains the same elements combined together in the same proportions by weight.

Chemistry is a branch of science that calls for concise and exact expression. This has been attained largely by the introduction of a simple but very ingenious system of **symbols**, leading in turn to a species of chemical shorthand for representing the make-up of the molecule of any particular substance. The elements are denoted by characteristic letters, such as H (hydrogen), O (oxygen), N (nitrogen), C (carbon), Fe (iron, *ferrum*), etc. Strictly interpreted, the symbol represents one atom of the element concerned. A molecule of hydrogen, containing two atoms, is written H_2; a molecule of water vapour becomes H_2O; and a molecule of calcium carbonate (chalk or marble) is represented by the so-called molecular formula, $CaCO_3$. The **molecular formula** gives the name and number of each kind of atom present in the molecule.

Some Common Elements

It is of interest at this point to take a bird's-eye view of the elements that figure most prominently in the chemistry of explosives; a dozen of them are given below, the first half-dozen being non-metals and the others metals:

Element	*Symbol*	*Atomic Weight*	*Element*	*Symbol*	*Atomic Weight*
Hydrogen	H	1	Sodium	Na	23
Nitrogen	N	14	Potassium	K	39
Oxygen	O	16	Calcium	Ca	40
Chlorine	Cl	35·5	Iron	Fe	56
Carbon	C	12	Mercury	Hg	201
Sulphur	S	32	Lead	Pb	207

SYMBOLS AND ATOMIC WEIGHTS

Hydrogen, nitrogen, oxygen, and chlorine are gaseous elements. *Hydrogen*, the lightest substance known, is colourless, odourless, and inflammable; it has the phenomenally low boiling-point of –253°C., and is very difficult to liquefy; when burnt in air it combines with oxygen to form water, of which it constitutes one-ninth by weight. *Nitrogen* is a colourless, odourless and inert gas, boiling at –196°; it is the chief constituent of the atmosphere, of which it forms about four-fifths; unlike oxygen, it does not support life or combustion. *Oxygen* is also a colourless and odourless gas, which boils at –183°; it constitutes eight-ninths by weight of water, and about one-fifth of the atmosphere, of which it is the active ingredient, since it supports both life and combustion. *Chlorine* does not occur uncombined in nature; it is a greenish-yellow, poisonous gas with a pungent odour; it may be readily condensed to a liquid, and then boils at –34·5°.

The last two non-metallic elements in the list are solids, and both are combustible. *Carbon* occurs in crystalline forms as diamond and graphite, and is still more familiar in the amorphous or non-crystalline state as soot, lampblack, charcoal, and gas-carbon. *Sulphur* is a yellow crystalline solid; unlike carbon, it melts easily when heated.

Of the metals, *sodium* and *potassium* are closely-related "alkali metals"; they are soft, silvery solids, which oxidise rapidly in the air and decompose water vigorously with the liberation from it of hydrogen; their reactions are dominated by their eagerness to combine with oxygen. Sodium is the metal of common salt, caustic soda, and washing soda; potassium is the metal of caustic potash, saltpetre, and chlorate of potash. *Calcium*, a hard silvery metal, is also affected by air and water in a similar way to sodium and potassium, but more slowly; it is the metal of lime, chalk, marble, and bleaching powder. *Iron*, *mercury*, and *lead*, unlike the three foregoing metals—which were first isolated in the uncombined state in the nineteenth century—have been known from very early days, and are familiar to everybody. Mercury (quicksilver) is the only metal that is liquid at the ordinary temperature.

Metals differ from **non-metals** in various physical and chemical properties: for example, they possess metallic lustre; they are

malleable, ductile, and good conductors of heat and electricity; chemically, they give rise to salts in conjunction with acids—marble is the calcium salt of carbonic acid, washing soda the sodium salt of carbonic acid, and saltpetre the potassium salt of nitric acid.

Earth, Air, Fire and Water

It may be mentioned that the so-called "elements" of the ancient Greeks and the alchemists—namely, earth, air, fire and water—are not elements in the modern sense of the term. Earth is a complex and variable mixture of substances; fire is the name given to the heat and light accompanying burning; water is a definite compound of oxygen and hydrogen; dry air is a mixture of gases composed on an average of 78·03 per cent. by volume of nitrogen, 20·99 per cent. of oxygen, 0·95 per cent. of inert gases (argon, helium, etc.), and 0·03 per cent. of carbon dioxide. Ordinary moist air contains about 1 per cent. of water vapour, and this proportion may be increased fourfold in warm humid climates.

How to Write Chemical Equations

Chemical reactions are expressed in this very convenient chemical shorthand by means of **chemical equations**, in which the substances used are shown on the left and those produced on the right. For example, when a mixture of hydrogen and oxygen is ignited, a chemical reaction takes place, and water is produced. This reaction is represented by the following equation:

$$2H_2 + O_2 = 2H_2O.$$

Thus, two molecules of hydrogen react with one molecule of oxygen to produce two molecules of water; this is the complete chemical process, no other substance being formed. Provided that the atomic weights (H = 1, O = 16) are known, the equation shows also that 4 units by weight of hydrogen combine with 32 units of oxygen to yield 36 units of water: thus, 4 grams (or lbs.) of hydrogen combine with 32 grams (or lbs.) of oxygen to yield 36 grams (or lbs.) of water (whether weighed as ice, water, or steam). As matter is indestructible, the atoms and weights on one side of the equation must exactly balance those on the other.

A chemical equation may be interpreted not only in terms of weight, as above: when the substances concerned in the change are gaseous it shows in addition the volumetric relationships between them. Any molecule of any substance in the gaseous state, no matter how much or how little it weighs, occupies the same volume under similar conditions of temperature and pressure. Thus, in equations dealing with gases, the numbers of reacting molecules may be read off also as the numbers of reacting volumes. The equation $2H_2 + O_2 = 2H_2O$, for example, expresses the observed fact that two volumes of gaseous hydrogen combine with one volume of gaseous oxygen to yield two volumes of steam, if all the volumes are measured at the same temperature and pressure; in this particular instance, of course, the volume of the gaseous product can be observed only if the experiment is conducted at a temperature above the boiling-point of water. Taking the reverse process, the decomposition of water into its elements is represented by the equation, $2H_2O = 2H_2 + O_2$, and this agrees with the familiar fact that when water is decomposed by electrolysis the volumes of hydrogen and oxygen produced are in the ratio 2 : 1.

How to Write Thermochemical Equations

When hydrogen and oxygen combine to form water much energy is set free in the form of heat. This so-called **heat of reaction** is expressed in the following **thermochemical equation** (Greek, *thermos*, hot):

$$2H_2 + O_2 = 2H_2O \text{ (gas)} + (2 \times 57{,}800) \text{ g.-cals.}$$

By halving this equation it is seen that 2 grams of hydrogen combine with 16 grams of oxygen, with the production of 18 grams of water, in the form of steam, and the liberation of 57,800 gram-calories of heat. The equation also expresses the fact that the **heat of formation** of water from its elements is 57,800 calories per gram-molecule. A *calorie*, or gram-calorie (g.-cal.), is the amount of heat required to raise 1 gram of water through 1°C.; a kilogram-calorie (kg.-cal.), sometimes known as a *large calorie* is equal to 1000 gram-calories. A *gram-molecule* (sometimes called a *mol*) of any substance is its molecular weight expressed in grams:

thus, a gram-molecule of water (H_2O) is 18 grams, and of carbon dioxide (CO_2) 44 grams. The heat of formation of carbon dioxide is 94,400 gram-calories per gram-molecule:

$$C + O_2 = CO_2 + 94{,}400 \text{ cals.}$$

Heat-giving and Heat-taking Compounds

Most compounds give up heat when formed from their elements; but there are some that absorb heat in these circumstances. Compounds of the first type, with a positive heat of formation, such as water and carbon dioxide, are called **exothermic**, or heat-disbursing:

$$2H_2 + O_2 = 2H_2O \text{ (gas)} + (2 \times 57{,}800) \text{ cals.} \quad . \quad (1)$$

If the heat of formation is negative, as with acetylene (C_2H_2), the compound is said to be **endothermic**, or heat-absorbing:

$$2C + H_2 = C_2H_2 - 54{,}300 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

According to this equation, the combination of 24 grams of carbon and 2 grams of hydrogen to form a gram-molecule (26 grams) of acetylene is attended by the absorption of 54,300 calories.

Sometimes compounds cannot be built up directly from their constituent elements; but in such cases the heat of formation can be determined indirectly. It is found that exothermic compounds are much more stable, and much harder to decompose, than endothermic compounds. This difference can be readily understood by referring to the typical examples of water and acetylene.

The thermochemical equation for the decomposition of the exothermic substance, water, into its elements is as follows:

$$2H_2O \text{ (gas)} + (2 \times 57{,}800) \text{ cals.} = 2H_2 + O_2 \quad . \quad (3)$$

Water can be broken down into its elements only by restoring to it, as heat or some other form of energy (such as electrical energy), an amount of energy exactly equivalent to the heat it gave up when formed, as shown in equation (1). Every gram-molecule (18 grams) of water requires 57,800 calories of heat (or its equivalent in some other form of energy) to decompose it completely: thus, water has a high chemical stability.

On the other hand, the thermochemical equation for the decomposition of acetylene:

$$C_2H_2 = 2C + H_2 + 54{,}300 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

shows that a large amount of heat—exactly equivalent to the heat it absorbed when formed, as shown in equation (2)—is liberated when the molecule disrupts. In other words, the molecule of acetylene is a storehouse of energy, and the absorbed energy has to be given back when the structure breaks down. Often an initial impulse, caused by heat, shock, detonation (p. 58), etc., is sufficient to start the decomposition of an endothermic substance, and the internal molecular energy then comes into play and accelerates the process.

It will be noticed that Nature keeps a strict thermochemical balance-sheet. The heat disbursed when water is formed (equation 1) has to be supplied in exact measure when the same amount of water is decomposed (equation 3). Similarly, the heat absorbed when acetylene is formed (equation 2) has to be exactly disbursed when the same amount of acetylene is decomposed (equation 4).

To sum up: exothermic compounds disburse energy when they are formed, and absorb it when they are decomposed; endothermic compounds absorb energy when they are formed, and disburse it when they are decomposed. These thermochemical considerations are of primary importance in the chemistry of explosives.

How many Hands has an Atom?

As stated above, the molecular formula of a substance shows the nature and number of each kind of atom in the molecule. For example, the molecule of sulphuric acid is represented by H_2SO_4 and contains 2 atoms of hydrogen, 1 of sulphur, and 4 of oxygen; similarly, the molecular formula of nitric acid is HNO_3, and that of toluene is C_7H_8. For many purposes it is necessary to expand the molecular formula into a **structural formula**, which attempts to provide a picture of the way in which the constituent atoms of the molecule are associated, or linked together.

According to the **Theory of Valency**, advanced by Frankland in 1852, every atom is endowed with a definite combining

capacity, or valency. The behaviour of the hydrogen atom, for example, suggests that it possesses one point only at which attachment to another atom may take place: in other words, the chemical affinity of the hydrogen atom appears to be concentrated into one unit or parcel. This is expressed by saying that the hydrogen atom has a valency of 1. This unit combining capacity of the hydrogen atom may be represented by the symbol H· or H–, the dot or dash standing for a single valency, or point of attachment to another atom. The molecular formula of hydrogen (H_2) may therefore be expanded into the structural formula H·H, or H–H.

The linking of the two constituent atoms of the hydrogen molecule by means of a so-called *single bond*, H–H, may be illustrated in a pictorial way by imagining the hydrogen atom as a diminutive being possessing one hand. When two such atomic individuals meet, they clasp hands and remain in an attitude of permanent greeting:

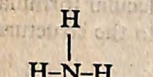
"And here's a hand, my trusty fiere,
And gie's a hand o' thine;
And we'll tak' a right guid-willie waught
For auld lang syne."

These hydrogen atoms have no second hand with which to indulge in further social activities. Chlorine also may be depicted as a one-handed atom: when it greets another chlorine atom with "Hail, fellow, well met!" and an extended hand, it forms with the second atom a molecule of chlorine, Cl-Cl. Alternatively, it may prefer to greet an atom of hydrogen, thereby giving rise to a molecule of hydrogen chloride, H-Cl, or H·Cl.

The oxygen atom has a valency of 2, with twice the combining —or hand-shaking—capacity of the hydrogen atom: it may thus be represented with two hands, as –O– or ·O·. When it clasps an atom of hydrogen with each hand it forms a molecule of steam (H_2O), which may thus be represented by the structural (or graphic) formula, H–O–H, or H·O·H.

Sometimes an atom can exhibit more than one valency value, depending upon the nature of the other atoms with which it is directly linked. It then behaves, in fact, as if it could put some of

its hands into common use and keep the others in its pockets, except upon special occasions. The nitrogen atom behaves like this. Upon meeting hydrogen atoms it offers three hands to them, but no more; each of the favoured hydrogen atoms clasps hands with the nitrogen atom, and the little party of four atoms form a molecule of ammonia, NH_3. The nitrogen atom holds two other hands in reserve, and these come into use in the formation of nitric acid and certain other nitrogen compounds:



Ammonia, NH_3

Nitric acid, HNO_3

In chemical language, the nitrogen atom has a valency of 3 in combination with hydrogen, but this value may rise to 5 when oxygen atoms are brought into direct attachment to the nitrogen atom. The two *double bonds* shown in the structural formula of nitric acid may be interpreted in each case as a double hand-shake between nitrogen and oxygen atoms.

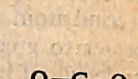
The carbon atom has a valency of 4, irrespective of the nature of the elements with which it is linked. The four-handed atoms of carbon are therefore able to enter into a great many social engagements, particularly as they have the greatest aversion to keeping any of their hands out of action in their pockets. Some simple types of their multitudinous combinations are shown below:

Methane, CH_4

Ethylene, C_2H_4

Acetylene, C_2H_2

Carbon tetrachloride, CCl_4



Carbon dioxide, CO_2

The double bonds in carbon dioxide show the carbon atom indulging simultaneously in double hand-shakes with two oxygen atoms, while in ethylene two carbon atoms are fraternising in a similar way and entertaining two hydrogen atoms each at the same time. The two carbon atoms of acetylene, with its

triple bond, have fallen into a friendship which appears almost too effusive to be lasting: this is actually the case, as acetylene is a distinctly unstable compound, which may break down with explosive violence when the atoms become excited.

Of the metals mentioned above, sodium and potassium are one-handed (valency 1, chlorides NaCl and KCl); calcium is two-handed (valency 2, chloride $CaCl_2$); iron may be either two-handed or three-handed (valency 2 or 3, chlorides $FeCl_2$ and $FeCl_3$); and mercury and lead are usually two-handed, although one of mercury's hands sometimes slips into a pocket (valency 2 or 1).

Molecules possessing double or triple bonds (especially in the chemistry of carbon compounds) are said to be *unsaturated*. Thus, ethylene and acetylene are unsaturated, since the carbon atoms are not provided with the maximum allowance of hydrogen atoms; methane, however, is saturated, because in no circumstances could its carbon atom combine with any additional hydrogen atoms. Saturated compounds are in general more stable and less reactive than unsaturated ones.

The number of chemical compounds occurring in nature is very large. These are supplemented by a vast and ever-increasing number of purely artificial compounds prepared in the course of scientific research. The total number of compounds capable of existence is, indeed, practically unlimited. The atoms of the known elements may be pictured as an alphabet of some 90 letters. This atomic alphabet may be utilised in the formation of molecules, corresponding to words formed from the ordinary alphabet of 26 letters. A consideration of valency and molecular structure shows that molecule-making, like word-making, conforms to certain rules: the atoms, like the letters, cannot be arranged in any haphazard number or order. Nevertheless, even when this restriction is borne in mind, it is easy to realise from such an illustration the almost unbounded variety of combinations which is possible in the molecular world.

Carbon, Glorious Carbon

One element—carbon—stands out from all the others, by reason of the prodigality with which it gives rise to compounds,

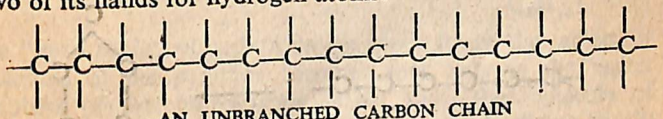
particularly in its manifold combinations with hydrogen, oxygen, and nitrogen. Carbon compounds are so numerous, indeed, that their study has given rise to a distinct branch of chemistry known as organic chemistry. Apart from their enormous variety, carbon compounds play a unique rôle in the chemistry of the life processes of plants and animals. It was on this account that, towards the end of the eighteenth century, substances occurring in, or produced from, inanimate mineral matter came to be known as **inorganic**, while those found in association with living, or "organised", matter were named **organic**. At the present day, **organic chemistry** is synonymous with the chemistry of the carbon compounds. It embraces not only the chemistry of the enormous number of carbon compounds found in living organisms (*e.g.* urea, glucose, egg-white), but also of the still larger number of purely artificial carbon compounds (*e.g.* chloroform, saccharin, trinitrotoluene). It was formerly supposed that a so-called "vital force" was necessary for the production of the natural carbon compounds, but this idea has proved to be wrong. The artificial synthesis in 1828 of urea, and also of alcohol in the same year, was gradually followed by the purely artificial preparation of hosts of other organic compounds produced in living plant and animal organisms.

As an example of the phenomenal manner in which carbon gives rise to derivatives, its hydrides, or compounds with hydrogen, may be cited. Some elements form no hydrides at all, and few form more than two or three: chlorine, for example, forms only one, known as hydrogen chloride, HCl; oxygen forms two, known as water (H_2O) and hydrogen peroxide (H_2O_2). The known hydrides of carbon—the so-called hydrocarbons—number several thousand, and thousands more are capable of existence, and could be synthesised if required.

Reverting now to the picture of carbon atoms as diminutive four-handed beings, it can be said that their social activities are unrivalled in the whole world of atoms. This is due only in part to their four-handed nature, because there are other kinds of atoms having as many as six or seven hands and yet endowed with only a rudimentary social instinct. The unique characteristic of carbon atoms is their unequalled capacity for fraternising among them-

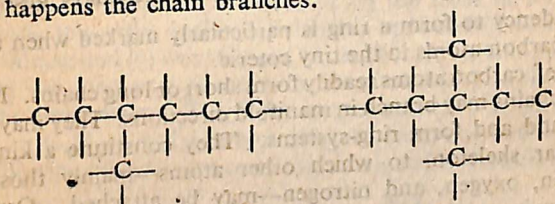
selves. Atoms of other elements exhaust their powers of mutual hand-clasping by the time that three or four of them, at the most, have joined in. Carbon atoms, on the contrary, enter into this form of association with the utmost zest, keeping at the same time their friendly contacts with other atoms, notably those of hydrogen, oxygen, and nitrogen. One carbon atom offers two of its four hands to two fellows; each of these reciprocates, and waves a spare hand to other carbon atoms . . . hand-clasp follows hand-clasp, until a long chain of dozens, or even scores, of these diminutive beings has been formed, after the manner of a line of life savers on the beach at Manly or Bondi.

In the simplest form of this chain, each carbon atom reserves two of its hands for hydrogen atoms:



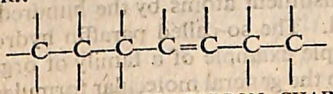
AN UNBRANCHED CARBON CHAIN

Sometimes, however, a particularly social atom will offer its third—or even its fourth—hand to another carbon atom. When this happens the chain branches:



BRANCHED CARBON CHAINS

Sometimes, also, two carbon atoms indulge in a double handshake, and this leads to the formation of a double bond somewhere in the chain:

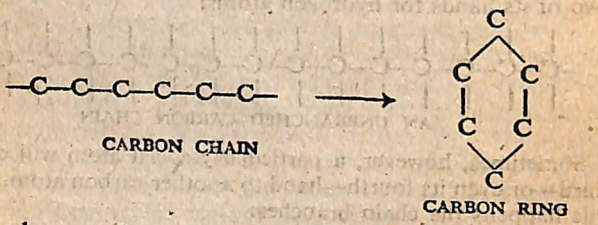


AN UNSATURATED CARBON CHAIN

If the disengaged hands (shown by strokes) are wholly seized by

hydrogen atoms, the resulting compounds are hydrocarbons. They contain nothing but carbon and hydrogen. Sometimes, however, oxygen or nitrogen atoms slip in and take part in the hand-clasping, thereby giving rise to alcohols, aldehydes, acids, esters, amines, nitro-compounds, and many other types of organic compounds. These ideas are embodied in Kekulé and Couper's **Theory of Molecular Structure** (1858), upon which organic chemistry rests.

Occasionally, as these restless chains of carbon atoms twist and twine in snake-like motion, the two atoms at the ends of the chain join hands, thereby forming a ring of atoms, which may be depicted as dancing in gay abandon around a molecular mulberry bush:



CARBON CHAIN

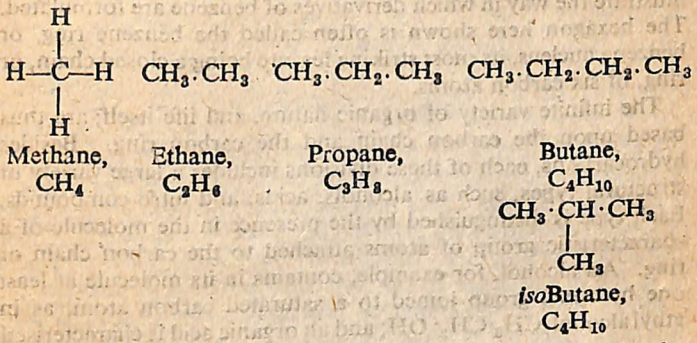
CARBON RING

The tendency to form a ring is particularly marked when there are six carbon atoms in the tiny coterie.

In brief, carbon atoms readily form short or long chains. These carbon chains may branch in manifold directions. They may also curl round and form ring-systems. They constitute a kind of molecular skeleton, to which other atoms—mainly those of hydrogen, oxygen, and nitrogen—may be attached. Organic chemistry is mainly the chemistry of carbon in combination with hydrogen, oxygen, and nitrogen.

The great complexity which organic molecules may assume is largely determined by the above factors. Some of these molecules number their constituent atoms by the hundred and others even by the thousand. The so-called paraffin hydrocarbons may be quoted as a simple example of a family of organic compounds. They conform to the general molecular formula C_nH_{2n+2}, giving rise to what is known as a *homologous series*, in which n may have any value from unity to about 60, or even higher. The structural

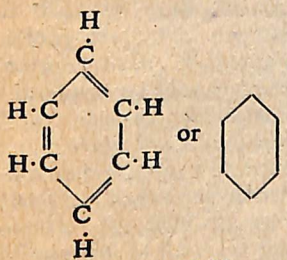
formulæ of the members having $n = 1, 2, 3$ or 4 are given below:



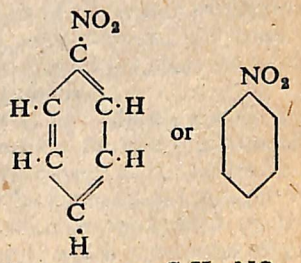
Methane, CH_4 — Ethane, C_2H_6 — Propane, C_3H_8 — Butane, C_4H_{10} — *iso*Butane, C_4H_{10}

The "open chain" of carbon atoms which forms the molecular backbone of the paraffins becomes very long in the higher members of this homologous series: thus, the molecule of triacontane, $C_{30}H_{62}$, contains an unbranched chain of 30 carbon atoms, and its structural formula may be written briefly, $CH_3 \cdot (CH_2)_{28} \cdot CH_3$.

Organic compounds are classified on the basis of molecular structure, the main divisions being (*a*) **open-chain**, or **aliphatic** compounds, and (*b*) **closed-chain**, or **ring** compounds. Prominent among the ring compounds are the **aromatic compounds**, or **benzene derivatives**. The fundamental aromatic compound is benzene, C_6H_6, a hydrocarbon obtained from coal tar, to which the following molecular structure was assigned by Kekulé in 1866:



Benzene, C_6H_6



Nitro-benzene, $C_6H_5 \cdot NO_2$

The structural representations of nitro-benzene are added to illustrate the way in which derivatives of benzene are formulated. The hexagon here shown is often called the benzene ring, or benzene nucleus, its most striking feature being a closed chain, or ring, of six carbon atoms.

The infinite variety of organic nature, and life itself, are thus based upon the carbon chain and the carbon ring. Besides hydrocarbons, each of these divisions includes a large variety of structural types, such as alcohols, acids, and nitro-compounds. Each type is distinguished by the presence in the molecule of a characteristic group of atoms attached to the carbon chain or ring. An alcohol, for example, contains in its molecule at least one hydroxyl group joined to a saturated carbon atom, as in ethyl alcohol, $CH_3 \cdot CH_2 \cdot OH$; and an organic acid is characterised by the carboxyl group, $-\overset{\overset{O}{\|}}{C}-OH$, as in acetic acid, $CH_3 \cdot COOH$.

A molecular grouping of great importance in the chemistry of explosives is the nitro group, $\cdot NO_2$, or $-N\begin{matrix}O\\O\end{matrix}$ which occurs for instance in the molecule of nitro-benzene (MNB) shown above. This group is almost invariably derived from nitric acid, HNO_3, or $HO \cdot NO_2$, which is therefore a reagent of primary importance in the manufacture of explosives.

CHAPTER III

WHAT ARE EXPLOSIVES?

Exothermic Reactions

MANY chemical changes are attended by the liberation of energy, in the form of heat, light, etc. Such processes provide examples of **exothermic reactions**. Sometimes heat is liberated so rapidly that a flame results, as in the burning of a candle or of a jet of hydrogen. Burning, or combustion, whether of a candle, hydrogen, wood, coal, or any other material which takes fire in air, is a consequence of rapid *oxidation*, or combination with oxygen. When the combination with oxygen is slow, as for example in the rusting of iron, the heat of reaction is dissipated before it is able to raise appreciably the temperature of the immediate environment.

It may be shown, however, that a large quantity of heat is liberated in the rusting of iron, as is evident from the following thermochemical equation:

$$4Fe + 3O_2 = 2Fe_2O_3 + (2 \times 190{,}700) \text{ cals.}$$

The rapid burning of magnesium ribbon is much more spectacular than the slow rusting of iron, owing to the manifestation of heat and light in the former reaction; yet, weight for weight, iron liberates nearly 30 per cent. as much energy as magnesium, upon oxidation.

In these two examples the products of the highly exothermic reactions are solid. A further consideration of the highest importance in the chemistry of explosives comes into play when the products are gaseous, or partly gaseous.

When gaseous hydrogen is burnt at an ordinary gas-jet, the resulting flame has a high temperature; but the reaction is unable to spread beyond the immediate environment of the orifice, and the heat is quickly dissipated through the surrounding atmosphere. Moreover, the intensity of the reaction is moderated by the diluting effect of the inert gas, nitrogen, which constitutes about four-fifths of the air—of which only about one-fifth is oxygen.

A strikingly different effect is achieved when a mixture of hydrogen with half its volume of oxygen is submitted to the passage of an electric spark in a closed glass flask (protected by a cover of copper gauze, as shown in Fig. 1). Both chemically and thermochemically, the reaction is identical in these two experiments:

$$2H_2 + O_2 = 2H_2O + (2 \times 57{,}800) \text{ cals.}$$

In the second experiment, however, the effect is much more violent than in the first. The combination of the intimate mixture of hydrogen and oxygen, started by the spark, spreads almost instantaneously throughout the mixture; the equally rapid liberation of the total heat of the reaction raises the gaseous product to a high temperature, and the consequent sudden expansion causes the containing flask to be shattered to a fine powder, with a loud report (*see the warning on p.* 34). In common parlance, the mixture explodes. The maximum effect is attained when the two gases are mixed in the exact proportion demanded by the equation for the oxidation of hydrogen.

A confined mixture of methane (marsh gas) and oxygen may be made to give a similar result, the maximum effect being reached in this case when the methane is mixed with twice its volume of oxygen:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 210{,}800 \text{ cals.}$$

The methane-oxygen explosion is more violent than the hydrogen-oxygen one, since both the volume of the gaseous product and the heat of combustion are greater with the hydrocarbon than with hydrogen.

"Firedamp" explosions in coal mines are caused by the ignition of mixtures of methane and air: air containing any proportion of methane between 5 and 13 per cent. is explosive. Indeed, all gaseous or vaporised hydrocarbons form explosive mixtures with air or oxygen, and for this reason it is necessary to avoid the vaporisation of petrol and similar materials in a garage or other enclosed space.

The explosion of mixtures of oxygen with hydrogen or gaseous hydrocarbons is tantamount to a very rapid combustion in an enclosed space. The resulting water and carbon dioxide, being

highly exothermic compounds, are raised to a very high temperature at the moment of their formation; a high pressure is generated, and this in turn leads to the disruptive effect.

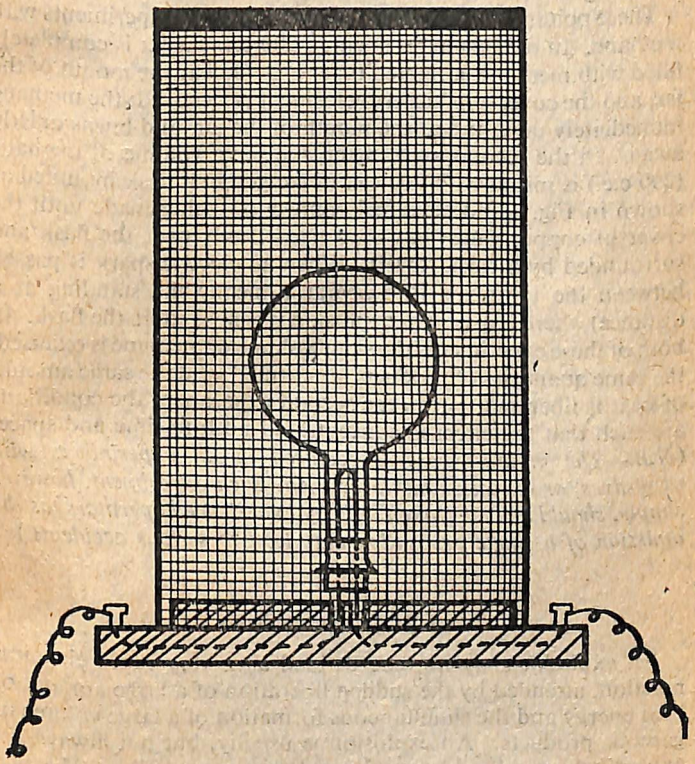


FIG. 1.—THE EXPLOSION OF MARSH GAS AND OXYGEN

In these instances an explosion takes place only when oxygen and the gaseous hydrocarbon are present in favourable proportions in a confined space. The maximum effect is reached when the actual proportions are those required by the corresponding

equation. If air is used as the source of oxygen, the unreactive nitrogen exerts a damping effect on the reaction by diluting the explosive mixture. Unless the gaseous mixture is subjected to some degree of confinement, no explosion results.

These points may be illustrated by two simple experiments with methane. In the first experiment, a 200 c.c. gas-jar is completely filled with methane, a lighted taper is held near the mouth of the jar, and the cover-slip hitherto closing it is removed: the methane immediately takes fire at the mouth of the jar, and burns quietly away. In the second experiment, the same volume of methane (200 c.c.) is mixed with 400 c.c. of oxygen in a flask mounted as shown in Fig. 1 (no electrical connection being made until the cover of copper gauze has been fixed firmly over the flask and surrounded by a thick towel). When an electric spark is passed between the terminals (the operator meanwhile standing at a distance), there is a violent explosion which shatters the flask. In both of these experiments the same volume of methane is oxidised, the same quantities of products are formed, and the same amount of heat is liberated; but in the second experiment the conditions are such that the effect is concentrated both in time and space. (*N.B.—The greatest care is required in all experiments with explosives, or explosive mixtures. Any such experiment, however simple, should be undertaken only by experienced operators, as the omission of a single precaution may lead to serious accidents.*)

An Explosion Defined

An **explosion** may now be defined as a very rapid chemical reaction, attended by the sudden liberation of a large amount of heat energy and the simultaneous formation of a large volume of gaseous products. An explosion is usually, but not always, an exceedingly rapid oxidation, burning, or combustion. The two fundamental equations for oxidative explosions are shown below, the carbon and hydrogen being, however, initially in the combined state, as in methane, petrol, etc.:

$$C + O_2 = CO_2 + 94{,}400 \text{ cals.}$$
$$2H_2 + O_2 = 2H_2O \text{ (gas)} + (2 \times 57{,}800) \text{ cals.}$$

So far, only the explosion of gaseous mixtures has been considered. Explosions of this type are comparatively mild, and may be applied under control as sources of power in the internal combustion engine, to move a piston against an external load. Such gaseous mixtures are not sufficiently powerful for use as industrial or military explosives, quite apart from the fact that solid or liquid materials are much easier to transport and handle than gases.

Enormously more powerful effects are produced in the explosion of suitable liquids or solids, owing largely to the greatly enhanced expansion in these instances. In the methane-oxygen explosion the expansion is due entirely to the heat effect: at constant temperature the original mixture of 1 volume of methane and 2 volumes of oxygen produces 1 volume of carbon dioxide and 2 volumes of steam, the total volume remaining unaltered. But when solid gunpowder explodes it produces about 500 times its own volume of gases, measured at the ordinary temperature, increasing under the expansive action of the liberated heat to about 4000 volumes. The corresponding volumes of gases formed from 1 volume of exploding liquid nitro-glycerine are approximately 1200, expanding to 10,000. Thus, 1 c.c. of nitro-glycerine is capable of generating, within a small fraction of a second, about 10 litres of an intensely hot gaseous mixture, reaching a temperature of some 3000°C.

An Explosive Defined

These considerations show that an **explosive** may be defined as a material capable of developing a sudden high pressure by the rapid formation of large volumes of gases at a high temperature. In all explosive processes at least part of the products must be gaseous, so as to be able to do work by expansion: the heat energy of liquid or solid products cannot act effectively in this way.

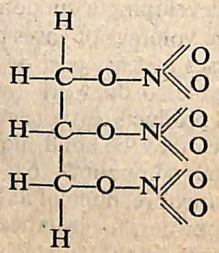
Explosives themselves may be solid, liquid, or gaseous; they may also be individual compounds or mechanical mixtures. When an explosive is a mixture, none of its ingredients need be an explosive in itself: gunpowder, for instance, is a mixture of charcoal, sulphur, and saltpetre, none of which is explosive singly.

Oxidative Explosions

In gunpowder, the necessary oxygen is supplied in a combined form by the saltpetre, which is also known as nitre or potassium nitrate (KNO_3). Solid mixtures of the gunpowder type and gaseous mixtures of the methane-oxygen type contain their oxygen atoms in one kind of molecule and their oxidisable atoms in other kinds of molecules. It is evident that a much more intimate and effective juxtaposition would be secured by arranging to have both kinds of atom within the same molecule. This is the state of affairs in all oxidative explosives of high power, such as nitro-glycerine. In nitro-glycerine, which is an individual compound having the molecular formula $C_3H_5O_9N_3$, the oxygen atoms are present in the same molecule as the carbon and hydrogen atoms which they are destined to oxidise in the explosive process. A more intimate preliminary association of the oxidising and oxidisable atoms cannot be conceived.

It is a curious fact that explosives are usually dependent for their existence upon the element nitrogen—an inert gas which enters into chemical combination only with great reluctance, and retires from such distasteful gregariousness into "splendid isolation" at the first opportunity. Nitrogen acts, in fact, as a buffer element in the molecules of nitro-glycerine, trinitrotoluene, picric acid, and the numerous other explosives of the kind. The function of the nitrogen atoms is to hold away the oxygen atoms (or most of them) from the carbon and hydrogen atoms until the signal for the molecular Armageddon arrives.

The molecular picture of nitro-glycerine afforded by its structural formula is given below:



Nitro-glycerine, $C_3H_5O_9N_3$

The signal for the disintegration of this molecular microcosm may be given by detonation, shock, or rapid heating. When it arrives, the unwilling nitrogen atoms throw off the oxygen shackles. The unstable oxygen-nitrogen linkages undergo sudden disruption. The simultaneous union of the atoms of carbon and hydrogen with those of oxygen, accompanied by the liberation of an enormous amount of heat energy, leads to the almost instantaneous production of a very large volume of gaseous products, giving rise in turn to the characteristic shattering effect. The ideal equation (*cf.* p. 53) for this explosion is as follows:

$$4C_3H_5O_9N_3 = 12CO_2 + 10H_2O + 6N_2 + O_2 + (4 \times 432{,}400)\text{cals.}$$

This equation shows clearly that the explosion of nitro-glycerine is a kind of internal, or intramolecular, burning; this proceeds with an almost inconceivable rapidity and fierceness.

The necessary nitrogen atoms are almost always introduced into the molecules of explosives by means of nitric acid. This indispensable reagent in the explosives industry was formerly prepared almost exclusively by distilling sodium nitrate, obtained from naturally occurring Chili saltpetre, with sulphuric acid. At the same time, Chili saltpetre was one of the chief sources of "fixed", or combined, nitrogen for use as a chemical fertiliser for plants. These natural deposits of crude sodium nitrate, although of vast extent, were within measurable reach of exhaustion early in the present century, when various chemical processes were elaborated for the fixation of atmospheric nitrogen, in such forms as nitro-lime, or calcium cyanamide ($CaN \cdot CN$), ammonia (NH_3), and nitric acid (HNO_3). The fixation of atmospheric nitrogen is nowadays an essential process in the manufacture of explosives, and as such it played a rôle of primary importance in the war of 1914-1918; it is also of fundamental importance in the provision of nitrogenous fertilisers for the soil.

Non-oxidative Explosions

It must not be concluded that explosions are necessarily the result of rapid oxidation. Some explosive compounds, such as lead azide (PbN_6) and benzene diazonium chloride ($C_6H_5 \cdot N_2 \cdot Cl$) contain no oxygen at all. Others contain neither oxygen nor

nitrogen, acetylene (C_2H_2) being an example of this kind. Any compound capable of swift decomposition with the liberation of heat and the formation of gaseous products may act as an explosive. Acetylene is a highly endothermic compound (p. 21), and in such a case there is no need to generate heat by oxidative processes as with the exothermic compound, nitro-glycerine. In certain circumstances, as for example when detonated (p. 58) under slight pressure, acetylene decomposes with explosive violence into a very hot mixture of fine soot and gaseous hydrogen:

$$C_2H_2 = 2C + H_2 + 54{,}300 \text{ cals.}$$

At sufficiently low temperatures acetylene may be liquefied by the application of pressure, and in this form its explosive effect is greatly intensified owing to the preliminary concentration in volume. The metallic acetylides, such as silver acetylide (C_2Ag_2), are violent explosives: since they are solids, their chemical energy has also been concentrated into a small volume.

Besides its intrinsic explosive property, which is independent of oxygen, acetylene, like all gaseous hydrocarbons, forms explosive mixtures with air. The range of such dangerous mixtures is unusually wide, since it includes all proportions of acetylene from 3 to 82 per cent. Acetylene can thus take part in both non-oxidative and oxidative explosions.

Physical Explosions

As a rule, explosions are the result of chemical change, and in the foregoing discussion they have been considered solely from this customary point of view. It must be added, however, that the term "explosion" is quite often applied to sudden disruptive processes of a purely physical nature. For example, bottles of ginger-beer exposed to hot sunshine, and cylinders containing oxygen gas stored under pressure, have been known to "explode"; boiler "explosions" are also of this type.

Such accidents to ginger-beer, oxygen cylinders, and boilers are not the result of chemical action, but are due entirely to physical causes. It is interesting that advances in the technique of handling liquefied gases has enabled this type of disruptive

process to be put to industrial use. Ordinarily carbon dioxide is a gas, but it may be liquefied under high pressure in strong containers: when the pressure is released, the substance reverts quickly to the gaseous form, thereby expanding rapidly to occupy a very much greater volume than before. Strong steel shells containing liquid carbon dioxide under a pressure of some 1500 lb. to the square inch are used for blasting purposes in the United States. A chemical heating element (consisting of sodium chlorate, aluminium and charcoal) situated inside the shell is ignited electrically: the sudden increase in pressure to about 9 tons per square inch bursts open the shell and brings about the blasting effect. Since this "explosive" consists entirely of carbon dioxide, which is non-combustible (and, indeed, a fire-quencher), it is particularly suitable for use in coal-mines.

It is an interesting reflection that carbon dioxide in its usual gaseous form is the antithesis of an explosive substance; and yet liquefied carbon dioxide, by virtue of its physical properties, could justifiably be termed an explosive. Similarly, water in liquid form is the very negation of explosibility; nevertheless, when suddenly gasified into superheated steam it is capable of creating spectacular disruptive effects. Chemical compounds, like human beings, are often the victims of circumstances.

CHAPTER IV

HOW EXPLOSIVES GET THEIR ENERGY

The Importance of Being Energetic

IT is a fundamental maxim, embodied in a proverb, that one must eat to live. Life is dependent upon energy, and bodily energy is supplied by the regulated oxidation (or slow combustion) of food. The capacity to do bodily work is also dependent upon energy and therefore upon food-supply. Most of the work done by primitive man called for the direct and personal expenditure of muscular energy. Man, however, is a thinking animal, and he has never been over-fond of work. Thus, from the very dawn of civilisation he has economised his bodily effort in every conceivable way, as by the use of other animals, of slaves, of primitive implements, and of machines increasing from age to age in efficiency and complexity.

In his hunting and fighting activities, the primitive club and hand-thrown missile gave way during the passage of unnumbered centuries to the axe, sling, bow, dart, boomerang, and other simple weapons of the primitive savage. These devices were gradually improved, and mechanical energy began to replace muscular energy in such devices as the catapult and the crossbow. Man awoke to the possibility of harnessing the forces of nature to his needs, and began to extract natural energy from the winds to propel his ships, grind his corn, and pump his water. He found also that flowing water could be made to do work by turning water-wheels.

The Application of Chemical Energy

It was at a late stage in his development, however, that man discovered efficient ways of transforming chemical energy into mechanical energy. He had been familiar from very early times,

of course, with the spectacular phenomenon of burning and with various applications of the energy liberated in the forms of heat and light in this chemical process; but the effective use of the heat of a burning fuel as a source of motive power was a discovery of the late eighteenth and early nineteenth centuries, based upon the invention of Watt's form of the steam-engine.

The first effective use of chemical energy in imparting motion to bodies had come long before that period with the discovery, in the fourteenth century, of the propelling effect of gunpowder: here, the chemical reaction was a rapid combustion of the explosive type, and the moving body was a projectile. Thus, the application of chemical energy to the propulsion of missiles, in the fourteenth century, was not merely of interest in the development of methods of warfare, as generally supposed. It had a much wider significance. It marked the beginning of a new epoch in man's methods of utilising natural sources of energy. This is a point of fundamental importance which has hardly received the emphasis it deserves in the history of the development of science. Gunpowder, the first explosive, opened out a new way of storing and releasing energy. The echoes of the first artificial explosion, ringing down through the centuries from Roger Bacon's primitive laboratory, reverberate around us in ever-increasing volume in this modern age of explosives and internal combustion engines.

In tracing the ultimate source of the energy liberated in these explosive processes, now so familiar throughout the civilised world, it is helpful to make a classification of natural sources of energy in general. The two fundamental divisions of such energy are non-organic and organic.

Non-organic Sources of Energy

Of the non-organic sources of energy, winds have been used from very early times; but **boreal energy,** although useful, is capricious: the sail sags when the sound of the grinding is low.

Water power, derived mainly from the potential energy of high-level lakes and ice-fields, has reached a much higher degree of utilisation than wind power. Falling water, formerly used to

work water-wheels, is now applied to drive turbines; these convert the water power into electricity, a form of energy which may be readily conveyed through cables in order to light streets, drive trains, or work vacuum cleaners and electric razors in distant regions. So the waters of Niagara and the "white coal" of the high Norwegian ice-fields are now rivals of the brown coal of Germany and the black coal of South Wales as efficient sources of energy. It must be emphasised that water power depends upon the *position* of the water—that is, upon its perpendicular height above the turbines in the power station—and not upon its chemical composition. As the water loses height it gives up its potential energy, but chemically and physically it remains unchanged.

Hydraulic energy is sometimes transferred through electricity into heat for use in the manufacture of valuable chemicals. At Niagara, in Norway, and at Hobart and other favourable centres, closed electric furnaces are heated in this way to the very high temperature (3000°C.) necessary for the manufacture of calcium carbide from a mixture of lime and coke. Calcium carbide, in turn, is used in making acetylene, acetaldehyde, and alcohol, all of which play a part in the chemistry of explosives; moreover, when heated electrically to about 1100°C., calcium carbide combines with nitrogen to yield the familiar fertiliser and source of fixed nitrogen known as nitro-lime or calcium cyanamide.

Another method of fixing nitrogen through the intervention of hydraulic energy depends upon the direct combination of nitrogen and oxygen brought about by passing air through an electric arc at about 3000°C. This process has been likened to the natural fixation of nitrogen which takes place along the path of a flash of lightning in a thunderstorm—the flame of the electric arc having been pictured as artificial lightning. As worked at Notodden and Rjukan, in Norway, this process utilised hydraulic energy equivalent to about 350,000 horse-power. The cooled gases when sprayed with water yield nitric acid, which is used extensively in the manufacture of explosives. Thus, the energy of the intensely hot gases of a bursting shell may have been derived in part from a remote Norwegian ice-field.

Tidal energy offers another source of water power. This depends upon the difference of level caused by the rise and fall of

the tides, a rhythmic effect of the gravitational action of the moon and sun, and it has been utilised to a limited extent by the construction of tidal barrages in narrow channels.

In an address to the British Association for the Advancement of Science, in 1904, Sir Charles Parsons surveyed the possibility of tapping the **internal heat energy of the earth** by sinking a shaft twelve miles deep. He estimated that such an operation would take eighty-five years and cost £5,000,000, an amount which he characterised in 1919 as only the cost of one day of the war of 1914-1918 to Great Britain alone.

A further interesting possibility lies in the direct utilisation, by means of parabolic reflectors or other **sun-engines**, of the incessant stream of energy radiated to the earth from the sun. As a simple example, roof-installations have been used successfully in favourable latitudes for the provision of domestic hot-water supplies warmed directly by solar energy.

We have seen above that the most concentrated source of terrestrial energy now available at a moment's notice is given by explosive molecular disintegration. In such breakdowns the constituent atoms of the molecule retain their identity. In some instances, however, atoms themselves are known to undergo a spontaneous disintegration accompanied by the regular emission of large amounts of heat energy. Substances showing this kind of behaviour are said to be radio-active, the best-known example being the element radium. If **atomic disintegration** could be started and controlled artificially, like molecular disintegration, it would provide a new source of energy of incomparable magnitude and compactness. Our most violent explosions are rapid molecular disintegrations: the result of sudden atomic disintegration on a similar scale would be stupendous. Solar energy itself is now supposed to arise from a subatomic source through the combination at a very high temperature and pressure (possibly reaching twenty million degrees Centigrade and ten thousand million atmospheres) of atomic nuclei of hydrogen, in groups of four, to form atomic nuclei of helium, with a copious liberation of radiant energy. Perhaps it is fortunate that man, with his remarkable aptitude for misusing scientific discoveries, has not yet found it possible to release atomic energy at will.

A review of the various sources of non-organic energy shows that in all instances the sun acts as the ultimate fount of the energy concerned. Water power, for example, is traceable to the absorption of solar energy in evaporation: through this process water is raised from the surfaces of oceans and lakes to the sky, whence it falls as snow or rain upon the place beneath. The earth is constantly receiving solar energy at the rate of about 228 million million horse-power, but this stupendous amount is only a minute fraction ($4{\cdot}5 \times 10^{-10}$) of the sun's total output, nearly all of which is lost in the remote depths of interstellar space.

Organic Energy

Of all terrestrial sources of energy the commonest and also the most efficient is organic energy. This, again, is derived from solar energy. Organic energy is stored energy, abstracted from sunlight by means of chemical processes in which the green leaf plays the part of an energy transformer. The cells of the living leaf may be pictured as miniature chemical laboratories in which wonderful syntheses are accomplished with consummate ease. In these synthetic processes, atmospheric carbon dioxide and water, the burnt-out residues of plant and animal life, are reconditioned. With the aid of the radiant energy of sunlight these simple inorganic molecules (CO_2 and H_2O)—possibly in their combined form as carbonic acid (H_2CO_3)—are built up, in a series of chemical reactions known collectively as *photosynthesis*, into the complex organic molecules of carbohydrates, fats, proteins, etc., with progressive storage of energy.

These photosynthetic reactions need not be discussed in detail —and, indeed, they are by no means fully understood. To take a specific example, the formation of ordinary sugar in the sugar cane or sugar beet is the result of a series of chemical changes which may be summarised as follows:

$$12CO_2 + 11H_2O = C_{12}H_{22}O_{11} + 12O_2 - 1{,}349{,}600 \text{ cals.}$$

Processes of this kind, entailing the removal of oxygen, are denoted as *reduction* processes. Reduction is thus the reverse of oxidation. In the formation of organic matter it is always

accompanied by the absorption of energy. When the organic matter is oxidised, either slowly in the plant or animal organism or rapidly in an ordinary fire, the stored energy is liberated. The complete oxidation of cane sugar may be represented as below:

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O + 1{,}349{,}600 \text{ cals.}$$

Endothermic reduction and exothermic oxidation are complementary processes in the economy of nature.

A little reflection will show that the vital activities of plants and animals are dependent upon a constantly recurring cycle of chemical operations. Pictured as a whole, these activities may be likened to the rhythmic action of a great natural engine which may be symbolised in some such way as the following:

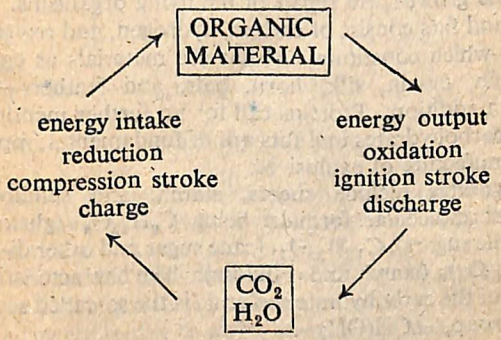


FIG. 2.—THE ORGANIC CYCLE IN NATURE

Organic energy is thus stored up in a chemical form in the carbohydrates, fats, and other substances produced by photosynthetic processes in the green plant. Animal life is dependent upon plant life for these sources of energy: all flesh is grass.

To sum up: all our energy is derived ultimately from the sun. It is applied mainly through the intervention of winds, high-level water, and organic material. Of these three immediate sources, the last is the commonest and most efficient. The sole source of vital energy and the chief source of chemical and mechanical energy is organic.

Carbohydrates, Fats, Coal, and Petroleum

The raw materials for the synthesis of the organic substances which act as the repositories of organic energy are carbon dioxide (of which the air contains 3 or 4 parts per 10,000), water (from the air and soil), and inorganic salts and nitrogenous compounds (in the soil). The agents are the radiant energy of sunlight and the living plant cell, the latter acting as an energy transformer. The finished products are carbohydrates, fats, proteins, and other types of organic compounds: these act as plant and animal foods, and in general as storehouses of chemical energy.

The three groups of organic compounds of outstanding importance in plant and animal life are the carbohydrates, fats, and proteins. These are necessary not only as sources of energy but also for the growth and repair of the living organisms. Carbohydrates and fats consist of carbon, hydrogen, and oxygen only. Proteins—which constitute such diverse materials as egg-white, hæmoglobin, casein, silk, horn, hair, and feathers—contain nitrogen in addition. Proteins call for no further mention here, but both carbohydrates and fats are of fundamental importance in the manufacture of explosives.

Carbohydrates include sugars, starch, and cellulose, the commonest molecular formulæ being $C_6H_{12}O_6$ (glucose and other simple sugars), $C_{12}H_{22}O_{11}$ (cane sugar and other di-sugars), and $(C_6H_{10}O_5)_n$ (starch and cellulose). The characteristic structural unit of the carbohydrate molecule is the so-called secondary alcohol group, $-CH(OH)-$.

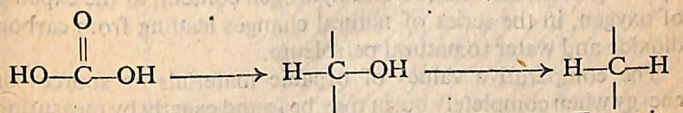
The group of **fats** includes all the "fixed", or non-volatile, fats and oils of plants and animals, such as olive oil, cottonseed oil, linseed oil, whale oil, butter, lard, and suet. Physically they range from liquid oils to hard fats; chemically they may be broken down by treatment with hot acid or alkali into glycerine (glycerol) and mixtures of fatty acids. This process is called the hydrolysis, or saponification, of fats and oils: the second name arises from the fact that the alkaline hydrolysis of fats and oils yields glycerine and soaps, the latter being sodium or potassium salts of fatty acids. The typical hard fat, tristearin, which is very similar to tallow (rendered suet), has the molecular formula $C_{57}H_{110}O_6$. Upon hydrolysis with hot dilute sulphuric acid this

molecule yields one molecule of glycerine, $C_3H_8O_3$, and three molecules of stearic acid, $C_{18}H_{36}O_2$:

$$C_{57}H_{110}O_6 + 3H_2O \text{ (in presence of acid)} = C_3H_8O_3 + 3C_{18}H_{36}O_2.$$

Tristearin — Glycerine — Stearic acid.

Fats are pictured as arising in the living organism through the reduction of carbohydrates, with a still further storage of energy in the molecule. Very little oxygen remains, the characteristic structural unit of the fat molecule being $-CH_2-$. The passage from carbonic acid through carbohydrates to fats consists of repeated reduction accompanied by a repeated uptake of energy:



Carbonic acid — Carbohydrate unit — Fat unit

As a source of energy in the animal organism it has been found that sugar may replace fat in the proportion of 2¼ parts of sugar for 1 part of fat.

Plant and animal organisms do not ordinarily store up energy in a more concentrated form than that of fats. In other ways, however, Nature is able to arrive at materials like petroleum and coal, from which all—or nearly all—of the oxygen has been removed, leaving only carbon and hydrogen. Natural petroleum, indeed, provides the most concentrated source of organic energy attainable. Coal is a heritage from primeval forests and jungles, the débris of which was probably subjected to bacterial decomposition under water, followed by exposure through long epochs to high temperature and pressure out of contact with air. Coal in its combustion may be said to liberate the solar glow which irradiated a prehistoric world. Petroleum was possibly formed in a somewhat similar way from the remains of both animal and plant life, notably perhaps from the remains of marine animal life.

The progressive replacement of oxygen by carbon and hydrogen

in the passage from carbonic acid (carbon dioxide and water) to petroleum is illustrated in the following table:

	Carbonic acid H_2CO_3	*Cane sugar* $C_{12}H_{22}O_{11}$	*A hard fat* $C_{57}H_{110}O_6$	*A bituminous coal*	*A petrol hydrocarbon* C_8H_{18}
Carbon	19	42	77	86	84
Hydrogen	3	6	12	5	16
Oxygen	78	52	11	8	0

TABLE OF PERCENTAGE COMPOSITIONS

The numerical data given in this summary are illustrated graphically in Fig. 3. This shows in a striking way the stepping-up of the combined carbon and hydrogen content, at the expense of oxygen, in the series of natural changes leading from carbon dioxide and water to natural petroleum.

The comparative values of organic materials as sources of energy when completely burnt may be found exactly by measuring the quantity of heat evolved when a standard weight of each is oxidised fully in a suitable apparatus. The following *heats of combustion*, or *calorific values*, relate to materials of the types under discussion; the petroleum contained 86·06 per cent. of carbon, 13·88 per cent. of hydrogen, and 0·06 per cent. of sulphur:

	G.-cals. per g.
Carbonic acid	0
Cane sugar	3946
Animal fat (average)	9500
Coal (dry, ashless)	9000
Pennsylvanian petroleum (crude) ..	10,840

CALORIFIC VALUES

Carbonic acid, being the final result of the complete combustion of all organic matter, has zero calorific value: it is totally "burnt out". As shown in Fig. 3, fats contain more oxygen than coal does, yet their calorific values are higher because they also contain more hydrogen than coal does; and, weight for weight,

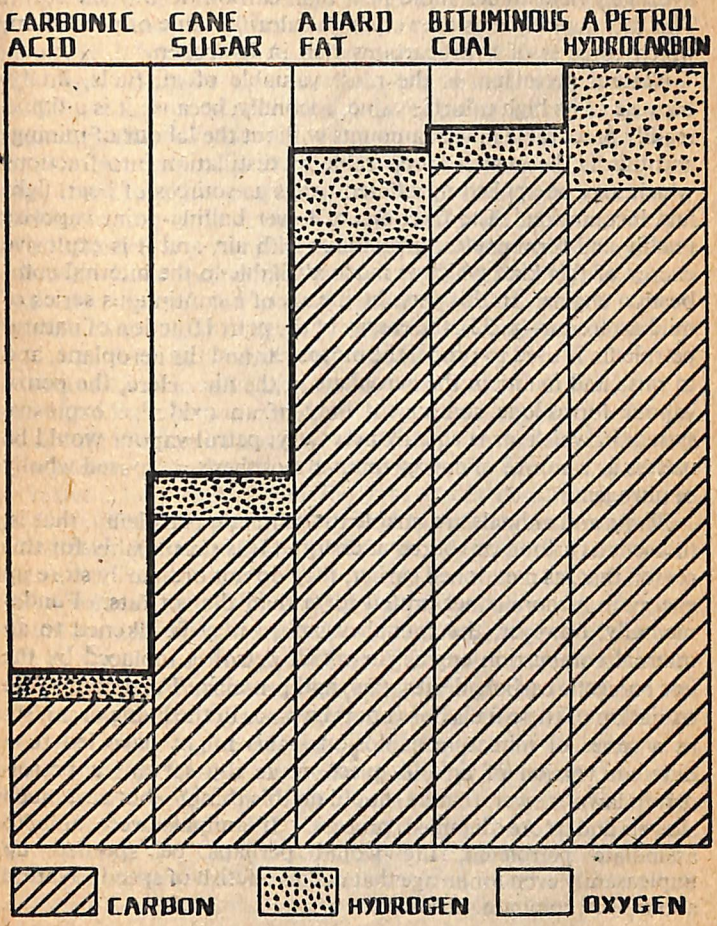


FIG. 3.—THE REPLACEMENT OF OXYGEN BY CARBON AND HYDROGEN

hydrogen yields much more heat than carbon does when burnt. This fact also explains the very high calorific value of petroleum, which consists of hydrocarbons rich in hydrogen.

Natural petroleum is the most valuable of all fuels, firstly, because of its high calorific value; secondly, because it is a liquid readily procurable in vast amounts without the labour of mining; and thirdly, because it is separable by distillation into fractions which may be applied in different ways as sources of heat, light and locomotion. The fractions of lower boiling-point vaporise readily and form explosive mixtures with air, and it is explosive energy of this kind which is made available in the internal combustion engine. In this way, by means of a continuous series of mild explosions (p. 35), the energy of the petrol fraction of natural petroleum is used to propel the motor-car and the aeroplane, and to raise and maintain the aeroplane in the air. Here, the petrol vapour forms one component only of an oxidative explosive system in which air is equally necessary: petrol vapour would be useless as a source of energy in an atmosphere composed wholly of nitrogen.

Plants and animals are unable to assimilate petroleum, that is, to use it as a food or source of energy. It is presumably for this reason that, as mentioned earlier, they do not ordinarily store up energy in a more concentrated form than that of fats. Fundamentally, however, the animal organism may be likened to an internal combustion engine, in which petrol is replaced by the less energetic carbohydrates, fats, and proteins. Fortunately, the oxidation of these fuels does not take place in the living organism as a series of miniature explosions—this might have led to a different version of an old question: Is thy servant a petrol-driven lawn-mower, that he should do this thing?—but as a much slower and more dignified process. If animals were able to assimilate petroleum, life would perhaps be speeded up unpleasantly even for an age that makes a fetish of speed. Nature abounds in common sense.

Fifth Columnists in the Molecular World

In her chemical mood, indeed, Dame Nature is a benign mother. Not content with endowing man with rich chemical

storehouses of food and energy, she has savoured his dishes with salt and spices, delighted his eyes with bright colours and his nostrils with fragrant perfumes, and has clothed him in garments of fibrous celluloses and proteins—her cottons and wools and silks. She has ordained, with a care hardly less than grandmotherly, that no natural beverage shall contain more than about 15 per cent. of alcohol; and even her poisons—her strychnine and morphine and atropine—have their beneficial uses. Finally, in her wisdom, she has refrained from including in her lavish chemical cornucopia any substance of an explosive nature.

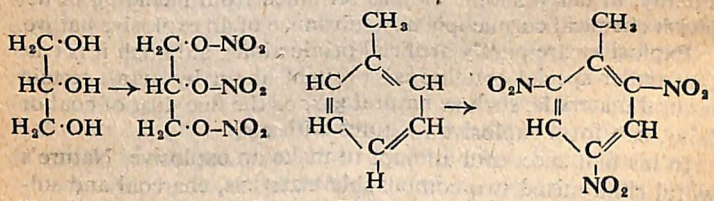
Explosives are purely artificial productions, although it is true that under special conditions—brought about by man—certain natural materials, such as natural gas, or the fine dust of coal or flour, can form explosive mixtures with air.

In his first successful attempt to make an explosive, Nature's wilful child mixed two combustible materials, charcoal and sulphur, with another substance, saltpetre, containing an abundance of oxygen in a condensed or combined form. The energy of the explosive is here derived from the three natural constituents of the mixture. Further, the mixture of the oxidising and oxidisable constituents is a mechanical one: in other words it is extra-molecular.

Not content with the power of his first explosive—gunpowder—man has turned to the concentrated organic energy of the carbohydrates, fats, coal, and petroleum, in fabricating the enormously powerful explosives of modern times. Into the molecules of substances derived from these sources, so stable and peaceful in their natural form, he has introduced a potential disintegrating influence in the form of nitro-groups ($-NO_2$). These nitro-groups infect the molecules with instability, by virtue of the relatively loose attachment of their constituent oxygen and nitrogen atoms. Nitro-groups are the fifth columnists of the molecular world. When the proper moment arrives they bring about the complete collapse of the molecular society into which they have insinuated themselves.

These molecular fifth columnists, or chemical agitators, attach themselves sometimes to oxygen atoms, as in glycerine and other alcohols, and sometimes to carbon atoms, as in benzene and

toluene. When they join to oxygen atoms the resulting explosive is a nitric acid ester of the alcohol, or alcohol nitrate, containing the bond O–NO_2; when they join to carbon atoms the product is a true nitro-compound with the bond C–NO_2. Examples of these two structural types are provided by "nitro-glycerine"—which is really glyceryl trinitrate, an ester of the alcohol, glycerol —and trinitrotoluene, a true nitro-derivative of the coal-tar hydrocarbon, toluene:



Glycerine — Nitro-glycerine (Glyceryl tri-nitrate) — Toluene — Trinitrotoluene (TNT)

The nitro-group is introduced in practice by treating the parent organic compound with a so-called "nitrating acid", or "nitrating mixture", consisting of a mixture of concentrated nitric and sulphuric acids.

It has already been pointed out that most modern explosives contain oxidising and oxidisable constituents within the same molecule. In such explosives the apposition of the elements, carbon, hydrogen, and oxygen is intra-molecular, and not extra-molecular as in gunpowder. The atoms of these three elements, straining "like greyhounds in the slips" upon the start of the sudden combustion, are held apart by atoms of the indifferent element, nitrogen. The molecules themselves are hybrid structures, containing oxygen-carrying nitro-groups grafted on to a natural molecular nucleus. In this way each molecule of the explosive is completely equipped: it is not dependent upon extraneous oxygen. When explosion occurs the molecule undergoes a sudden exothermic breakdown, as explained above (p. 37), the nitrogen being liberated as the free gaseous element. Modern warfare has

been described chemically as the rapid liberation on a large scale of gaseous nitrogen from organic combination.

"Open-cheque" and "Crossed-cheque" Energy

It is not commonly realised that the original natural compound, in its oxygen-containing environment, is a richer store of energy than the derived explosive. This must be so, however, because the introduction of nitro-groups brings about a "dilution" of carbon and hydrogen in the molecule, a point which is illustrated by the figures quoted below:

	C	*H*	*O*	*N*	*Heat of combustion (cals. per g.)*
Glycerine, $C_3H_8O_3$	39	9	52	—	4315
Nitro-glycerine, $C_3H_5O_9N_3$	16	2	63	19	1905
Toluene, C_7H_8	91	9	—	—	10,150
Trinitrotoluene, $C_7H_5O_6N_3$	37	2	42	19	3616

PERCENTAGE ELEMENTARY COMPOSITIONS AND HEATS OF COMBUSTION

The last column of the table shows that when 1 gram of nitro-glycerine is burnt completely it liberates only 44 per cent. of the amount of heat emitted similarly by 1 gram of glycerine. The chemical equations representing the complete combustion of glycerine and nitro-glycerine are written as follows:

$$2C_3H_8O_3 + 7O_2 = 6CO_2 + 8H_2O,$$
$$4C_3H_5O_9N_3 = 12CO_2 + 10H_2O + 6N_2 + O_2.$$

The explosion of nitro-glycerine is supposed to follow the equation for its complete combustion, and the energy liberated in this process does not exceed 44 per cent. of the energy of the parent substance, glycerine.

An even more striking example of this kind is provided by the coal-tar hydrocarbon, toluene, and its derivative, trinitrotoluene. The explosive furnishes upon complete combustion less than 36 per cent. of the energy given by the parent compound; here, too, the energy liberated upon explosion is much less, since trinitro-

toluene contains less than half the amount of oxygen necessary for its complete combustion:

$$4C_7H_5O_6N_3 + 21O_2 = 28CO_2 + 10H_2O + 6N_2.$$

The equation shows that 4 molecules of trinitrotoluene contain 24 atoms of oxygen and require 42 extra atoms of oxygen for complete combustion. In the explosive, or internal, burning of the substance this deficiency cannot be made up.

For the complete combustion of any organic compound each constituent carbon atom requires two atoms of oxygen, and every pair of hydrogen atoms require one atom of oxygen. But in explosive processes of the intramolecular type the molecule of the explosive must provide its own oxygen: it cannot draw upon atmospheric oxygen. In some explosives the proportions are more favourable than in others. Rather exceptionally, the molecule of nitro-glycerine contains a full supply of oxygen: it requires only $8\frac{1}{2}$ atoms for complete combustion, and is able to provide 9. Trinitrotoluene, on the other hand, requires $16\frac{1}{2}$ atoms of oxygen, of which it can provide only 6. Nitro-glycerine contains a slight excess of oxygen, and trinitrotoluene suffers from a large deficit: nitro-glycerine is therefore the more powerful of these two explosives. When trinitrotoluene explodes, part of its carbon is oxidised to carbon monoxide (CO), and much free carbon is liberated in the form of a thick black smoke: it was for this reason that shells filled with TNT were known in the war of 1914-1918 as "coal-boxes", or "Jack Johnsons" (after a celebrated negro boxer of the time).

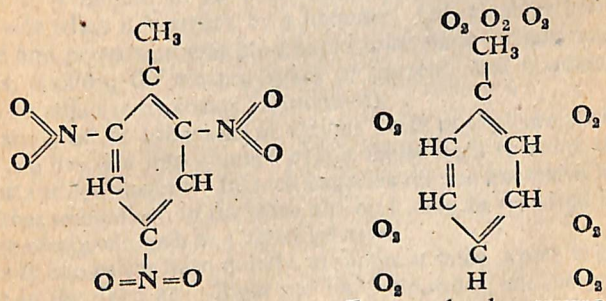
This analysis accounts largely for the difference in explosive properties shown by nitro-glycerine and trinitrotoluene, which in some respects are curiously similar: NG contains 20 atoms in its molecule, TNT contains 21, and each has the molecular weight 227.

The considerations advanced above should be sufficient to explode the popular fallacy that explosives provide phenomenal stores of energy as compared with other substances. To emphasise this point it may be added that there is far more energy stored up in a pound of butter than in a pound of trinitrotoluene, and that kerosene—although a much less spectacular oil than nitro-

glycerine—is capable of doing about seven times as much work, weight for weight.

At the same time it must be stressed, at the cost of repetition, that explosives differ from these more concentrated sources of organic energy in being self-contained. Coal, petroleum, toluene, butter, and the like, demand an environment containing oxygen before they can furnish energy. They are not self-contained sources. On the moon, with its lack of oxygen, motor spirit would have no more value than water as a source of energy, and coal no more than sand. Trinitrotoluene, on the other hand, would still be capable of releasing its full store of energy if it could be exploded on the moon.

The relationships and distinctions obtaining between such energy-sources as the explosive trinitrotoluene and its placid parent, toluene, may be summed up by likening both types to cheques drawn on the Bank of Energy. The cheque signed by the impulsive trinitrotoluene is an open cheque, payable anywhere, and without notice; but the cheque bearing the signature of the more cautious toluene is crossed "Payable only in an oxygen-containing atmosphere", and notice is required so that there is time to count out the coins. In the first case, the molecule is a self-contained source of energy with an intra-molecular oxygen supply; in the second, it is not self-contained, the oxygen supply being extra-molecular:



Intra-molecular oxygen. Extra-molecular oxygen.

TRINITROTOLUENE AND TOLUENE AS SOURCES OF ENERGY

To sum up: most of the modern explosives may be regarded as hybrid products, in which man has "disguised fair nature with hard-favour'd rage" by grafting disturbing nitro-groups on to the placid, energy-laden molecules of glycerine, cellulose, toluene, and the like. Explosive energy is thus chiefly organic energy, supplemented to some extent by hydraulic energy which may have been introduced in forming the nitro-groups. Further, the salient feature of an explosive is not that it contains a particularly large store of energy, but that it can unlock its energy swiftly and completely, with the production of gaseous products. The vast scale on which this swift and destructive liberation of energy may be achieved is well illustrated by Sir Charles Parsons' statement that all the guns of a battleship of the *Queen Elizabeth* class, if fired simultaneously, would for the instant be developing more than thirteen million horse-power.

CHAPTER V

MORE ABOUT EXPLOSIVES

The "Firing" of Explosives

For five hundred years after its first use as an explosive, gunpowder had no rival either for civil or military purposes. It stood alone. Throughout these centuries the explosive process was always started by bringing a flame, a spark, or a hot body, into contact with the powder at an exposed point, such as a touch-hole. Since a form of fire was the initiating agent, and the gunpowder exploded with a flash, the inception of the explosion became known as "the firing" of gunpowder. When other explosives were introduced in the nineteenth century, the term "firing" was applied to them in the same sense. It is, however, a popular fallacy that the application of a flame to an explosive always causes an explosion. Some explosives do not explode when ignited by a flame, and others may explode without being ignited: for instance, trinitrotoluene burns without exploding when it is ignited in an open space, and mercury fulminate explodes when it is struck by a hammer. Other agents besides flame and percussion may start explosions: these include heated solids, friction, the electric spark or current, and concussion from an adjacent explosion (detonation).

A study of the behaviour of various kinds of explosives when they are brought into contact with a flame leads to some very important conclusions. In such experiments the explosive may be either unconfined in the open air, or it may be enclosed in a strong receptacle such as a cartridge case.

Many explosives burn quietly, at different rates, when lit by a flame in the open air. These include gunpowder, cordite, gun-cotton, the coal-tar explosives (TNT, lyddite, etc.), and even nitro-glycerine and blasting gelatine in small quantities. Other

explosives, such as mercury fulminate and lead azide, explode with great violence when ignited under any conditions. These differences in behaviour may be traced to the relative speeds of the reactions concerned.

Speed is a factor of prime importance in explosive reactions. Although these reactions may appear to the human eye or ear to happen instantaneously, it has been shown by the use of delicate instruments that their velocities extend over a wide range. These differences in the speed of explosive decomposition are due not only to the chemical constitution of the explosive, but also to the conditions under which the explosion is started and to the method of starting it.

The explosion of gunpowder, like its quiet burning, is essentially a rapid combustion in which the ignition of one particle brings the temperature of adjacent particles to ignition point, thus enabling combustion to proceed throughout the whole mass. Under the most favourable conditions the speed of this reaction does not exceed 400 metres per second. A similar explanation accounts for the quiet burning of unconfined trinitrotoluene and other explosives.

Detonation

Even with explosives like mercury fulminate and lead azide there is an exceedingly brief period of slow burning; but this is followed by a rapid acceleration which culminates in a violent explosion accompanied by intense shock waves. Each shock wave forms an explosive front travelling through the mass of the explosive at a speed ranging from 3000 to 9000 metres per second. The temperature at the wave front may rise for a fleeting instant as high as 10,000° C. Such a shock wave, known also as a *detonation wave*, may even carry its explosive action across an air gap and activate a further mass of explosive on the farther side.

An explosion of this kind, brought about by a shock wave or detonation wave, is known as a **detonation** (Latin, *de* down, and *tonare* to thunder). Explosives which burn rapidly to detonation in the open are called **detonants.** In working practice they are

more usually known as **initiatory explosives** (p. 130). The best-known examples are mercury fulminate and lead azide. The small metal tubes containing such explosives in a compressed form are termed *detonators* (p. 144). Detonants are not necessarily explosives of outstanding power or sensitiveness, although those in common use have to be sensitive in order to fulfil their function. Each explosive has its own rate of detonation, but a detonation wave of the right speed may be imparted to it through contact with an appropriate exploding detonant, although the two rates of detonation are different. Thus, when trinitrotoluene is fired by a suitable detonator, instead of burning quietly it undergoes a complete molecular disruption caused by an explosive wave moving through it at a speed of 6700 metres (more than 4 miles) per second. Experimental methods have been elaborated for measuring the velocity of detonation, which is influenced by such factors as the density of the explosive and its temperature and degree of confinement.

Propellants and High Explosives

Some explosives, including gunpowder and cordite, besides burning quietly in the open, also burn away without detonating when they are ignited in strong confinement; others, although they burn quietly in the open, eventually detonate under the latter conditions.

Explosives like gunpowder and cordite, which burn without detonating even when strongly confined, may be used as **propellants,** or propelling explosives. In cartridges containing these propellants, the cap of a primer (p. 147) containing a suitable composition is fired by the impact of the firing mechanism, and the ensuing flash ignites the adjacent gunpowder. In cordite cartridges a small charge of gunpowder is often placed between the primer and the propellent charge, so that the primer ignites the powder and thence the cordite. The pressure of the explosion gases from a charge or cartridge of an explosive of this type is used to drive the bullet or shell along the bore of the weapon. An explosive capable, when confined under such conditions, of

burning to detonation cannot be used as a propellant, because the sudden pressure generated upon detonation would shatter the weapon.

This last kind of explosive is known as a **high explosive** (H.E.), or shattering explosive. High explosives are used for filling shells, bombs, torpedoes, and mines, and also for demolition work. They are characterised by the violence of their suddenly exerted disruptive effect, which is often referred to as *brisance*. The shattering effect of a high explosive is invariably obtained by detonation, since it demands the liberation of the energy of the explosive in the shortest possible time and in the highest possible concentration. High explosives differ a great deal in their sensitiveness to detonation. Thus, while blasting gelatine or dry guncotton respond invariably to detonation with mercury fulminate, the response of wet guncotton or block trinitrotoluene to the same detonant is uncertain. Detonation may be brought about in such instances by interposing a small amount of a third explosive between the detonator and the high explosive. The interposed explosive, which must of course be sensitive to the detonant, is called the "gaine",* "booster" or "exploder". Trinitrotoluene in block form may be successfully primed in this way with a little tetryl, or even with some of its own powder or fine crystals used as the gaine.

High explosives used as fillings for shells to be fired from guns must necessarily be very insensitive to shock or friction: such explosives are so stable that they usually call for the use of a gaine. For blasting purposes in mining, quarrying and tunnelling, however, more sensitive explosives, capable of direct detonation without a gaine, can be used with safety. Operations in "fiery" coal-mines, containing firedamp (methane), necessitates the use of so-called "safety explosives": these are relatively slow-acting high explosives in which the temperature of the explosion flame is lowered by the addition of heat-absorbing substances such as ammonium chloride, sulphate, or oxalate, and sodium chloride (p. 81). "Permitted" or "permissible"

* Strictly interpreted, this word refers to the sleeve or container in which the intermediate explosive is loaded (French *gaine*, sheath), and not to the explosive itself.

explosives for use in coal-mines are characterised by a small and relatively cool flame of explosion of short duration. The character and duration of the flame of mining explosives, and also of propellants and cap compositions, may be studied by photographic methods which have been specially elaborated for this purpose. So many high explosives are now known, many of them being mixtures, that it is not difficult to find a suitable one to fulfil any specific requirement.

Brisance and Power

"At noon to the Coffee-house, where, with Dr. Allen, some good discourse about physic and chemistry. And among other things . . . he tells me . . . that something made of gold, which they call in chemistry *Aurum fulminans*, a grain, I think he said, of it put into a silver spoon and fired, will give a blow like a musket, and strike a hole through the silver spoon downward, without the least force upwards." So wrote Samuel Pepys in his famous diary, on 11th November, 1663.

Aurum fulminans, or fulminating gold, is a highly sensitive explosive, formed when ammonia is added under certain conditions to gold compounds. In reality, of course, the downward blow in such experiments as that mentioned by Pepys must be matched by an upward blow of equal force; but the latter, being exerted against an elastic medium—namely, the atmosphere—is far less spectacular than its counterpart, delivered against a solid and very rigid support.

Formerly, explosives were classified, according to their power, as "high explosives" or "low explosives", the popular criterion of a "high explosive" being its ability to "strike downward" upon its support when exploding; a "low explosive", on the other hand, was said to "follow the line of least resistance". It is now realised, however, that no satisfactory classification can be effected on this basis, which refers to brisance rather than power. In practice, it is more convenient to classify an explosive as a **propellant**, a **high explosive**, or a **detonant** (or **initiator**), these terms being interpreted as just explained. This classification is based upon the general character of the explosive rather

than upon its power. Confinement increases the violence or brisance of an explosion; but while gunpowder has to be strongly confined in order to produce disruptive effects, the brisance of mercury fulminate is increased very little by such treatment.

A simple experiment (*see the warning on p.* 34) is sufficient to show the great difference in brisance between the slow-acting propellant, gunpowder, and a rapidly-detonating high explosive such as picric acid. The lids of two ordinary tins, about 4 inches in diameter, are supported on two iron tripods. A small heap of gunpowder, weighing rather less than a gram, is placed on one lid, and a similar quantity of an intimate mixture of about equal weights of picric acid crystals and litharge (mixed without friction) is heaped upon the other. The operator then adjusts a small and steady Bunsen flame below the middle of each heap in turn and retires to a safe distance of several yards. In a short time the gunpowder inflames with a slight puff, producing copious smoke; but there is no report, and the lid is not dented. On the other lid, the picric acid mixture detonates, exploding abruptly with a loud and sharp report; little smoke is produced, a large hole is riven in the lid, and the Bunsen flame is extinguished by the blast of the explosion. The picric acid develops its pressure so suddenly that the resulting mass of gas is able to use the overlying atmosphere as a supporting wall, thus gaining the purchase necessary for the exertion of a powerful blow downwards. With gunpowder, however, the gaseous products are liberated so much less rapidly that the atmosphere has time in which to make way for their passage and dispersal "along the line of least resistance" before any strong reaction can be exerted on the solid support. The different effects may be likened in the one instance to the rapid slap of a flat paddle upon the surface of a lake, and in the other to the gradual pushing of the paddle below the surface.

It is the sudden liberation into the atmosphere of large volumes of gas at high pressures that produces the phenomenon of "blast", large wads of air being displaced violently in various directions from the centre of explosion. Pockets of strong compression and suction are thereby created, the effect being due mainly to the displaced air and not directly to the gaseous products of the explosion.

Of various methods used for comparing the power of explosives, the **Trauzl Test**, or **Lead Block Test**, is perhaps the most convenient; but it is suitable only for strictly parallel tests made upon high explosives of the same type. The method depends upon measuring the distension produced by a standard weight (10 grams) of the explosive when it is fired in the bore-hole of a

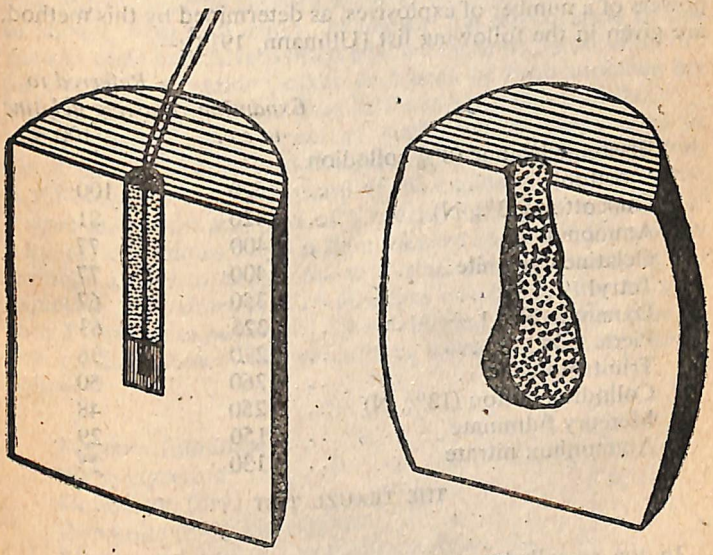


FIG. 4.—THE TRAUZL TEST
(Showing the Lead Block in vertical section before and after Explosion.)

lead block of specified dimensions. The block of pure soft lead (Fig. 4) is 200 mm. high and 200 mm. in diameter, and the central bore-hole is 125 mm. deep and 25 mm. wide. A 2-gram electric detonator is fixed into the middle of a cartridge formed by wrapping the explosive in tin foil; the cartridge is placed at the bottom of the cavity; this is then filled (tamped) with fine dry sand, and the charge is fired. The enlarged cavity is then cleaned

out, and its volume is found by filling it with water from a burette. Deductions are made for the original volume of the cavity (61 c.c.) and the expansion due to the detonator (17 c.c.), and the remaining volume represents the expansion due to the explosive. The mean value of at least three experiments is taken. Although the Trauzl block is no larger than a 15-lb. truckle of Cheddar cheese, it weighs about 156 lb. The relative powers of a number of explosives, as determined by this method, are given in the following list (Ullmann, 1914):—

	Expansion in c.c.	*Referred to Blasting gelatine =100*
Blasting Gelatine (8% collodion cotton)	520	100
Guncotton (13% N)	420	81
Ammonal	400	77
Gelatine dynamite	400	77
Tetryl	350	67
Dynamite No. 1	325	63
Picric acid	290	56
Trinitrotoluene	260	50
Collodion cotton (12% N) ..	250	48
Mercury fulminate	150	29
Ammonium nitrate	130	25

THE TRAUZL TEST

In the so-called **mortar test** the distance to which a 15-kg. shot is propelled under standard conditions by 10 grams of the explosive is determined. A third kind of test makes use of a special form of **ballistic pendulum.**

The Relative Sensitiveness of Explosives

The sensitiveness of explosives varies enormously. Whereas a rifle bullet may be safely fired into a solid mass of trinitrotoluene, it is said that a crystal of nitrogen iodide has been known to

explode when a fly used it as a landing-ground. The French chemist, Dulong, who discovered the closely related substance, nitrogen trichloride, in 1811, suffered the loss of an eye and three fingers in his researches on this very susceptible explosive.

No satisfactory general method is available for comparing the sensitiveness of explosives. The order of sensitiveness of a series of explosives varies according to the influence brought into play: thus, nitro-glycerine is more sensitive to heat, but less sensitive to impact, than lead azide. Moreover, the sensitiveness of one and the same explosive is often affected by its physical condition: for example, crystalline cakes or blocks of trinitrotoluene are more difficult to detonate than its loose crystals or powder.

The relative sensitiveness of explosives to **percussion,** or direct blows, is usually determined by the **falling weight test.** A thin layer (0·05 to 0·1 gram) of the explosive is spread upon a steel anvil, forming part of a special machine. A weight of 2 kg. (or sometimes 5 kg.) is then released so as to fall vertically through a known height on to a steel plunger overlying the explosive. The shortest fall which fires or explodes the charge is then found by experiment. The published results obtained by this method show wide variations; some of them are given below:

FALLING WEIGHT TEST (2 KG.)

	cm.
Mercury fulminate	2
Nitro-glycerine	4
Guncotton (dry)	5 to 10
Dynamite (25% kieselguhr)	7
Blasting gelatine (7% collodion cotton)	12
Picric acid	25
Trinitrotoluene	57 to 90
Black powder	70
Dinitrobenzene	200

The sensitiveness of explosives to friction, heat, and detonation must also be taken into account and subjected to appropriate tests. In general, too high a degree of sensitiveness is undesirable,

since very sensitive explosives are dangerous to handle, transport, or store. On the other hand, an explosive must be sufficiently sensitive to explode or detonate readily and completely under standard conditions. It may be added that under the British Explosives Act of 1875, explosives are arranged in seven classes, according to their proneness to ignition by fire, friction, chemical decomposition, and other causes.

CHAPTER VI

THE OLDEST EXPLOSIVE

The Romance of Gunpowder

THE oldest and most famous of all explosives is gunpowder. Much has been written about the origin of gunpowder; but much remains unwritten. It is strange that a discovery which had such a tremendous historical significance is as hard to pin down as the origin of a folk-song. Such a comparison is unusual; but gunpowder has this at least in common with folk-songs, that it seems to have been elaborated gradually by a series of unknown artists living in different countries at different times.

Fuming, fiery and flaming compositions of many kinds ("wild-fire") were known and used long before the introduction of gunpowder. These consisted of mixtures of such ingredients as charcoal, sulphur, resins, fats, and natural petroleum, pitches and bitumens. The celebrated Greek fire, used in the Byzantine period, was probably a composition of this kind. It is easy to imagine that enterprising experimenters would not fail to try the effect of adding familiar mineral materials to these mixtures, and so eventually the particular virtue of saltpetre would be recognised. The action of hot saltpetre on charred wood is spectacular, as the hero of *Lorna Doone* records in his description of how he did "John Ridd his name" in winkeys on his desk at school: "the fire of candle lays hold of the peter with a spluttering noise and a leaping. Then should the pupil stir bravely, and he will see a glow as of burning mountains, and a rich smoke, and sparks going merrily; nor will it cease, if he stir wisely, and there be good store of peter, until the wood is devoured through, like the sinking of a well-shaft."

The use of inflammable mixtures for producing fire and smoke

in warfare was described and pictured (Fig. 5) so late as 1540 in Biringuccio's *Pirotechnia*. The ingredients in use at that time included Greek pitch, powdered sulphur, lard, mineral oil, turpentine, saltpetre and gunpowder. The containers were earthenware pots, thrown by hand or with a sling; sometimes, too, linen bags were used for attaching the inflammable material to fiery arrows.

Two names are prominent in accounts of the early history of gunpowder—those of Roger Bacon of Ilchester in Somerset, and

FIG. 5.—FIRE-POTS AND FIERY ARROWS
(From Biringuccio's *Pirotechnia*, Venice, 1540)

Berthold Schwarz, of Freiburg im Breisgau. Roger Bacon is a definite historical figure of the first magnitude in the history of science; but Berthold Schwarz remains shadowy and enigmatical. In the little church at Ilchester, in 1914, a modest brass tablet was affixed to one of the walls to commemorate the seventh centenary of Roger Bacon's birth, "by a few admirers of his genius", who hailed him across the gulf of years as "brother, Englishman and friend". This bears an inscription which may serve as a sketch in outline of the earliest of the great scientists of England: "To the Immortal Memory of Roger Bacon, a Franciscan Monk and also a free enquirer after true knowledge. His wonderful

powers as mathematician, mechanician, optician, astronomer, chemist, linguist, moralist, physicist, and physician gained him the title of *Doctor Mirabilis*. He first made known the composition of gunpowder, and his researches laid the foundations of modern science. He prophesied the making of machines to propel vessels through the water without sails or oars; of chariots to travel on land without horses or other draught animals; of flying machines to traverse the air. He was imprisoned, starved and persecuted by the suspicious ignorance of his contemporaries, but a fuller knowledge now acclaims and honours him as one of

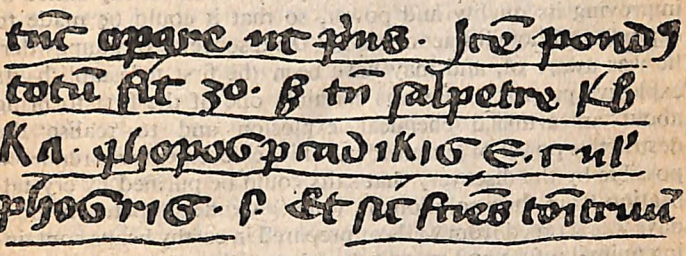


FIG. 6.—ROGER BACON'S GUNPOWDER ANAGRAM
(British Museum, Sloane MS. 2156)

the greatest of mankind. Born at Ilchester in 1214. Died at Oxford in 1294." (Plate IA.)

It was in his tract entitled, *De Mirabili Potestate Artis et Naturae* ("On the marvellous power of art and nature"), written in 1242, that Bacon "made known" the composition of gunpowder. The information was not stated in plain Latin, because of the importance of a secret so marvellous and revolutionary in its character. The operative sentence, which runs as follows, contained a concealing anagram (shown here in italics): ". . . Sed tamen salis petrae *luru vopo vir can utri* et sulphuris; et sic facies tonitruum et coruscationen, si scias artificium." According to Col. H. W. L. Hime, the eighteen letters of this cryptic expression

should be transcribed as, "R. VII PART. V NOV. CORUL. V", and expanded into, "recipe vii partes, v novellae coruli v". The sentence then reads: ". . . But of saltpetre take 7 parts, 5 of young hazel-twigs, and 5 of sulphur; and so thou wilt call up thunder and destruction, if thou know the art". Mystics will perhaps discover, in addition, an allusion in this cypher to the Gunpowder Plot of 5th Nov.! The original manuscript of Bacon's tract is unknown, but there is a version in the British Museum (Sloane MS. 2156) which contains a more complex form of the anagram (Fig. 6).

There is no justification for regarding Roger Bacon as the discoverer of gunpowder. His experiments evidently aimed at improving its quality and power, so that it could be made to explode. Although Bacon was not the discoverer of gunpowder, he was aware of, and may have been the first to establish, its explosive property. He was certainly one of the first to bring about an artificial chemical explosion and to realise the destructive power of gunpowder. This achievement was rendered possible by the discovery that salts could be purified by crystallisation from their solutions in water. Crude saltpetre in those days was scraped from walls or prepared in earthy heaps containing animal refuse and wood-ashes: it was therefore very impure. The earlier "gunpowders", made from such saltpetre, would be fiery or incendiary compositions which would fume and smoulder without exploding. From Bacon's time onwards, the saltpetre was purified by repeated crystallisation from hot water: Plate II is a 15th-century illustration showing how water was wrung out of recrystallised saltpetre contained in a long sack. Bacon also appreciated the importance of mixing the ingredients thoroughly in making gunpowder.

There is no evidence that Roger Bacon was acquainted with the propellent power of gunpowder or with its use in guns. The discovery that exploding gunpowder could exert a propelling force and drive a body through the air is usually ascribed to a mysterious monk, known as Berthold Schwarz, Bertholdus Niger, or Black Berthold. He is said to have been a Franciscan monk at Freiburg im Breisgau, in which city he is commemorated by a statue. His secular name is sometimes given as Constantin

Anklitzen, and possibly he owed his sobriquet to his supposed knowledge of the black art and his imagined dealings with its chief patron. An attractive copper engraving of 1643 (Plate III) depicts him in his laboratory in the act of firing a charge of gunpowder by means of a flint and steel; the gunpowder is contained in a mortar, and the force of its explosion projects a block upwards into the air. An inscription describes the "worthy and ingenious Father Bertold Schwartz" as a "Franciscan monk, doctor, alchemist, and inventor of the free art of using firearms in the year 1380". Sometimes the date 1354 is given; but if Berthold Schwarz invented firearms he must have done so not very long after Roger Bacon's death, for there is an illustration of a primitive gun in a manuscript of 1325 (Plate IB); moreover, there was a powder-works at Augsburg in 1340, and both gunpowder and cannon were being manufactured in England in 1344, and probably earlier. In English military operations, it is said that guns and gunpowder were first used at the Battle of Crecy, in 1346; although, according to another reference, certain "crakys of war", apparently a form of cannon, were used in 1327 by Edward III against the Scots.

Black Berthold is therefore to some extent a legendary figure. That the discovery of the propellent force of gunpowder was regarded in the Middle Ages as something sinister and a manifestation of the black art is apparent from several pictorial representations of Berthold in which the devil occupies a prominent position in the background, as prompter, admirer, or director of operations. The central idea was no doubt bound up with the popular conception of a satanic environment characterised by flashes of fire and the smell of brimstone. The same note of suspicion and foreboding—unhappily justified to a large extent by later events—was struck in an inscription appended to Galle's engraving, made about 1570, of Stradanus' spirited drawing *Pulvis Pyrius* (Gunpowder). This depicts the interior of a cannon foundry; outside, the finished products are shown in the act of demolishing the tower of a fort; and an inset shows Berthold Schwarz in his laboratory. The Latin inscription states "That thunders and thunderbolts should be brandished in the hand was surely given to us by the powers below".

Shakespeare—who seems to have imagined that saltpetre was a mineral obtained by mining—also gave voice to this attitude towards the discovery of gunpowder, in his play *Henry IV*, when he made Hotspur's "popinjay lord" exclaim:

> "It was great pity, so it was,
> This villainous saltpetre should be digg'd
> Out of the bowels of the harmless earth,
> Which many a good tall fellow had destroy'd
> So cowardly; and but for these vile guns,
> He would himself have been a soldier."

The manufacture of gunpowder developed as an art rather than a science, and there are many attractive accounts and illustrations of the progress of this art during the centuries succeeding the crucial discoveries. One of the most interesting repositories of such information is the *Codex Germanicus* in Munich, dating from about 1350. This gives, for example, some of the rule-of-thumb tests for the purity of the ingredients of gunpowder, accompanied by fascinating illustrations which are strangely modernistic in style. One of these shows a man and his wife thrusting their hands into a barrel of saltpetre and licking their fingers somewhat gingerly: "When thou buyest or makest saltpetre and wilt find whether it be good or not, so thrust thine hand thereinto. If thine hand become damp, then it is not good; but if thine hand bide dry, then it is good. Also touch thine hand with thy tongue; if thine hand be salty, then the saltpetre is not good; but if thine hand be sweet, then it is good."

These early chemical practicants were keen observers, and they gathered together a good deal of useful empirical knowledge. They knew that molten saltpetre lost all its moisture, and the *Codex* contains directions for casting it. There is also in the *Codex* a description of an intriguing test for sulphur, with an appropriately quaint illustration:* "If thou wilt try whether

* Reproduced in Read's *Prelude to Chemistry* (Bell, London), with many other illustrations of interest in alchemy and historical chemistry.

sulphur be good or not, take a lump of sulphur in thine hand and lift it unto thine ear. If the sulphur crackle, so that thou hearest it crackle, then it is good; but if the sulphur keep silent and crackle not, then it is not good, and must be treated as thou shalt hear hereafter how it shall be prepared." Curiously enough, this primitive and unlikely test is a genuine one.

For charcoal-burning the wood of the lime or poplar was recommended. The proportions given in the *Codex* are 4 of saltpetre, "which must be really good and well refined", 1 of sulphur, and 1 of charcoal. For a long time after the introduction of gunpowder the mixing was done by hand in a mortar, but this operation was found so fatiguing that eventually the pestle was hung from a springy wooden lath. This simple device, a familiar detail in illustrations of alchemical interiors, was first depicted in the *Codex*. The stamp mill was introduced in the fifteenth century. Saltpetre (sal-petir) used for making gunpowder in Scotland cost 3d. an ounce in 1500, and sulphur (bryntstane) cost 8s. a stone: a multiplier of 3 or 4 must be applied to convey a rough idea of the modern equivalents of these amounts. It is not known when wet mixing, which improves the product so markedly, was introduced; but the resulting corned powder was mentioned in 1429.

For more than a century after its introduction, the strength of the powder was apt to prove too much for the cannon. They who stood by, in those early days which saw the ordnance "with fatal mouths gaping on girded Harfleur", took dangerous risks when "the nimble gunner with linstock now the devilish cannon touches". It was in such circumstances that a Scottish King—James II—was killed by the bursting of a bombard at the siege of Roxburgh Castle in 1460. Not until the end of the fifteenth century was an effective control of gunpowder achieved. From that time until the middle of the nineteenth century it held the field as the only known explosive of any practical value. Its use as a mining explosive appears to date from the early seventeenth century.

In modern countries at different times there have been considerable variations in the composition and also in the size of

grain of the gunpowders used. Some of the changes in English powders are shown in the table below:

Date	*c.* 1250	1350	1560	1647	1670	1742	1781
Saltpetre	41·2	66·6	50·0	66·6	71·4	75·0	75·0
Charcoal	29·4	22·2	33·3	16·6	14·3	12·5	15·0
Sulphur	29·4	11·1	16·6	16·6	14·2	12·5	10·0

THE COMPOSITION OF ENGLISH POWDERS (AFTER HIME).

The first of these powders is Roger Bacon's. The second, made by Dr. John Arderne of Newark, contained the same proportion of saltpetre as the *Codex* powder of the same date. It will be seen that the general tendency has been to increase the proportion of saltpetre at the expense of the charcoal and sulphur. The powder of 1781 had the same composition as ordinary black powder of the present day. In England there were powder-mills at Waltham Abbey so long ago as the days of Queen Elizabeth, when powder-making was proclaimed a royal monopoly.

The use of gunpowder in firearms underwent a revolutionary change as a consequence of the invention, about 1814, of the percussion cap, primed with mercury fulminate. The introduction of ignition by percussion guaranteed a rapid discharge of the weapon, without the tedious use of flint and steel, or of the earlier and still more cumbrous slow-match, consisting in its primitive form of a piece of cotton, rope or tow steeped in a solution of saltpetre in lime-water. Until about 1880 gunpowder was the only propellant used in rifles and guns, but it has since been replaced for this purpose by smokeless powders (p. 110). As a propellant, gunpowder suffers from lack of power for modern requirements; it creates objectionably large volumes of a dense smoke; and it is damaged by wetting. These are drawbacks which have led to a great curtailment of its military uses; but it is still an essential explosive, both in peace and war. It is cheap and easily made, and besides being used extensively in bursting charges for shrapnel shell, primers for large charges of other propellants, and fillings for fuzes, it is in great demand for industrial, pyrotechnic, and sport-

ing uses: its manufacture is therefore carried out on a very large scale.

Getting the Ingredients

It is not surprising that the first explosive was a mixture of non-explosive ingredients of an inorganic character. Neither its invention nor its manufacture called for any real chemical knowledge. Although gunpowder contains carbon, this element is present in the free or uncombined condition, and not in organic combination. Of the three ingredients, **saltpetre** is present in the largest proportion. This is an inorganic salt, also known as nitre, or potassium nitrate (KNO_3). Wood-ashes, which contain potassium carbonate, provided the earliest source of potassium compounds. In Canada and Russia these ashes are still extracted with water, according to the ancient method; the residue from the evaporation of the clear solution is then calcined in iron pots, leaving "pot-ash", or impure potassium carbonate (K_2CO_3). Formerly, wood-ashes were the sole source of the potash (or, more correctly, potassium) constituent of saltpetre. Soil containing decomposing nitrogenous organic matter, such as urine, when mixed with wood-ashes, is found after a time to contain saltpetre, formed as a result of bacterial activity. If calcium carbonate—in the form of old mortar, for example—is substituted for wood-ashes in this process, calcium nitrate is formed. When lixiviated (extracted with water) and boiled with wood-ashes the product yields potassium nitrate in solution; this is filtered from the precipitated calcium carbonate and obtained by evaporation:

$$Ca(NO_3)_2 + K_2CO_3 = 2KNO_3 + CaCO_3.$$

Much potassium nitrate is made in this way in the Indian "nitre plantations".

The so-called "German", or "conversion", saltpetre is made by mixing Chili saltpetre (p. 37) with potassium chloride obtained from the natural Stassfurt deposits. During the cooling of a hot concentrated solution of equivalent amounts of these two salts, the sodium and potassium exchange their original partners, and the sodium chloride resulting from the "double decomposition"

crystallises out first, leaving the more soluble potassium nitrate in the mother-liquor, from which it may be obtained after further evaporation:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Since the introduction of processes for the preparation of nitric acid from atmospheric nitrogen (p. 42), it has become possible to prepare synthetic sodium nitrate by neutralising synthetic nitric acid with sodium hydroxide (caustic soda) obtained by the electrolysis of sodium chloride solution (brine). In all cases the potassium nitrate should be caused to separate in small crystals, so as to avoid inclusions of mother-liquor.

Sodium nitrate is easier to obtain, and therefore cheaper, than potassium nitrate; moreover, the sodium salt is a more concentrated source of nitrate oxygen, since the atomic weight of sodium (Na = 23) is less than that of potassium (K = 39). It is therefore unfortunate that sodium nitrate cannot ordinarily be used in making gunpowder, because it absorbs moisture from the air. This property of deliquescence is particularly evident in commercial specimens of the salt containing traces of calcium and magnesium nitrates and chlorides. Exceptionally, in the dry climate of Egypt, it proved possible to effect a marked economy during the construction of the Suez Canal by using a freshly-prepared mining powder in which potassium nitrate was wholly replaced by the cheaper sodium nitrate.

Charcoal for powder-making has to be prepared with much care. It was realised very early in the history of gunpowder that soft light woods gave suitable charcoals capable of ready ignition. Roger Bacon specified young hazel-twigs, and it is usual to select wood of from two to ten years' growth. Hazel wood is still used to some extent; but dogwood, willow and alder are now the chief woods. For a small-arm powder of small grain, which is required to burn quickly, dogwood charcoal is used; willow and alder are suitable for powders of coarser grain, burning more slowly. The fieriness of a gunpowder and its explosive power depend largely upon the mode of burning the charcoal: for example, quick-burning powders require porous, lightly-burnt charcoals. No charcoal is pure carbon, and gunpowder charcoals may contain

from about 75 to 85 per cent. of carbon, from 3 to 4 per cent. of hydrogen, and so much as 15 per cent. of oxygen. For high muzzle velocities the charcoal is burnt at comparatively low temperatures and has a correspondingly low carbon content. All gunpowder charcoals are required to burn freely and to reduce to a non-gritty powder.

Sulphur, otherwise brimstone (*brenne stone* or stone that burns), has been known for thousands of years. The native sulphur of the volcanic regions of Sicily was used by the Greeks and Romans, and Homer mentions its application as a fumigant. During the present century, however, Sicilian sulphur has been displaced to a large extent by sulphur obtained from the enormous deposits in Louisiana. These occur at an average depth of some 700 feet, with an overburden of clay, quicksand and rock. By the ingenious Frasch process the sulphur is brought to the surface in a rapid and economic way without the labour and expense of mining. Through a bore-hole four concentric pipes are sunk to the deposit. The two outer pipes act as jackets to the others, and through them superheated steam is forced at a temperature (155° C.) well above the melting-point of sulphur. By the action of compressed air in the innermost pipe the resulting molten sulphur is forced to the surface through the remaining pipe. The resolidified sulphur obtained in this way has a purity of 99·5 per cent., and may be used directly in the manufacture of sulphuric acid and many other important substances and materials, including gunpowder. The familiar "flowers of sulphur", a subsidiary product formed in the refining of Sicilian sulphur by distillation, cannot be used in making gunpowder, as this form of sulphur is contaminated with sulphurous and sulphuric acids; this objection does not apply to Sicilian roll-sulphur.

How Gunpowder is Made

In the manufacture of gunpowder the charcoal and sulphur are ground separately in suitable mills, the sulphur mill being carefully earthed so as to avoid any danger of ignition from sparks caused by an accumulation of static electricity. Charges of about

¾-cwt. of the three powdered ingredients, weighed out in the required proportions, are submitted to a first rough mixing in a mechanical mixer and then passed through a sieve before being brought into the incorporating mill. A primitive form of incorporating mill was mentioned by Biringuccio in 1540. In the modern mill the "green" charge is spread evenly on a circular iron bed some 7 feet in diameter. Here it is damped with distilled water and mixed thoroughly by a combination of runners and leather-covered wooden ploughs operated mechanically. If an accidental ignition occurs, an automatic apparatus drenches with water the contents of all the mills in the house concerned. The **milled cake** coming from the incorporating mill contains on an average about 2 per cent. of water if it is destined for small-arm powder and about double this amount for powders of larger grain.

The milled cake is reduced to a **meal** by gunmetal rollers fed from hoppers, the pressure being automatically limited to 56 lb. per sq. in. in order to avoid dangerous friction. The meal is then subjected to a pressure of about 400 lb. per sq. in. between earthed plates in a hydraulic press. After being broken up with wooden mallets the **press cake** obtained in this process is granulated.

In the important operation of **granulating**, or **corning**, the broken press cake is passed downwards through a system of inclined rollers and screens, so that the grains become progressively finer. The grains which pass a 10-mesh sieve and are held by a 20-mesh sieve are suitable for small-arm powders. Grains of unsuitable size are returned to the hoppers of the incorporating mill.

Dust is removed from the **grains** through a 20-mesh gauze in a rotating dusting-reel, and the grains are then polished by rotating them for several hours in large closed drums. With some powders the polishing effect of the consequent friction is aided by the introduction of a little graphite. The grains are submitted to a slow and even drying, by "stoving" them in shallow wooden trays for several hours in steam-heated rooms at about 40° C. In the "finishing" operation, carried out in a rotating canvas "reel", the dust formed in the drying is removed, and a final glaze is given to the grains. At various stages in the manufacture various

batches of powder are "blended", or mixed, so as to improve the uniformity of the ultimate product.

The Kinds of Gunpowder

It is often asked why gunpowder is made in grains, and not in powder as the name indicates. The chief reasons are that the processes of granulating and polishing reduce the tendency of gunpowder to absorb moisture and to form dust, while at the same time they increase its density and rate of explosion. Formerly, British service gunpowders were classified as R.F.G. or R.L.G. (rifled fine or large grain). A variety known as *pebble powder*, used in large guns before the introduction of smokeless powders, consisted of cubes cut from the press cake; *prismatic powder*, used in a similar way, took the form of hexagonal prisms of press cake, each with a central hole.

Ordinary black gunpowder contains 75 per cent. of nitre, 15 of charcoal, and 10 of sulphur, and in this form it is used for sporting purposes and also in mining and blasting. Sometimes the rate of burning of blasting powders is reduced by increasing the amount of sulphur at the expense of the nitre, as well as by increasing the size of the grains. Such mining powders, containing for example 20 per cent. of sulphur, give more gas but less heat than normal gunpowder. In a military modification known as *cocoa powder* or *brown powder*, used in guns of specially large calibre before the introduction of smokeless powders, the sulphur was reduced to 3 per cent., with 18 per cent. of a "caked cellulose" charcoal often made from straw and roasted only till brown.

Properties of Gunpowder

Since gunpowder is a mechanical mixture and not a single chemical compound, the properties of different specimens are subject to variation. That gunpowder is a mixture is readily shown by soaking it in water: the nitre dissolves, leaving the insoluble charcoal and sulphur behind, and the explosive property disappears. Gunpowders are heavier than water, the density ranging from about 1·67 to 1·87.

When heated, gunpowder explodes at about 300° C. In a vacuum, however, it is not fired by contact with a red-hot platinum wire. It is relatively insensitive to percussion (p. 65). It is a typical "low" explosive, and has to be strongly confined in order to produce a shattering or disruptive effect. In the Trauzl test gunpowder produces only about one-sixth of the expansion given by blasting gelatine under similar conditions (p. 64). On account of its low *brisance* it is a good explosive for blasting soft material into large masses. The chemical changes occurring in the explosion of gunpowder are often represented by the following equation, but in reality the decomposition is much more complex:

$$2KNO_3 + S + 3C = K_2S + 3CO_2 + N_2.$$

Other gaseous products include carbon monoxide (CO), sulphuretted hydrogen (H_2S), methane (CH_4), and hydrogen(H_2); while among the solid products are potassium carbonate (K_2CO_3) and potassium sulphate (K_2SO_4).

The volume of permanent gases varies considerably with the type of powder, but the heat of explosion increases as this volume decreases, so that the resulting pressures do not vary a great deal. Thus, in the following table the product of the two sets of numbers remains roughly constant:

Kind of powder	*Heat of explosion (cals. per g.)*	*Permanent gases (c.c. per g. at 0° and 760 mm.)*
Mining	517	360
Pebble	721	278
Large grain	726	274
Fine grain	738	263
Sporting	764	241
Cocoa	837	198

HEAT AND GAS IN GUNPOWDER EXPLOSIONS

The table shows that "what is lost in heat is gained in gas", and *vice versâ*. The temperature of the explosion reaches 2200° C. or even higher. The total potential energy of gunpowder has been

calculated at about 500 foot-tons per lb., but of this not more than about 20 per cent. becomes effective in a gun. The maximum velocity of explosion of gunpowder is about 400 metres per second.

Modified Gunpowders

In recent times a very large number of explosive compositions have been put forward which may be regarded as derived from ordinary gunpowder, although quite often they may contain no ingredient in common with it. *Bobbinites* may be mentioned as examples of compositions which still contain the three original constituents of gunpowder, with additions. They are modified black powders with a reduced temperature of explosion brought about by the incorporation of starch-wax granules or cooling salts, such as ammonium or copper sulphates, and they were formerly in use as "permitted" explosives for blasting in fiery mines. Various kinds of bobbinite may contain about 65 per cent. of potassium nitrate, 19 of charcoal, and 2 of sulphur, the remainder being either the above sulphates or a mixture of starch and paraffin wax.

Potassium nitrate is often replaced in such modified gunpowders by other salts rich in oxygen, such as sodium, barium and ammonium nitrates, potassium chlorate, and potassium, sodium and ammonium perchlorates. *Ammonal*, for example, is prepared in various forms, the chief constituent being ammonium nitrate; other ingredients are aluminium, charcoal, and sometimes trinitrotoluene. The mining explosive known under this name may contain about 95 per cent. of ammonium nitrate and 5 of aluminium, and a powerful blasting variety contains as much as 30 per cent. of trinitrotoluene, with 47 of ammonium nitrate, 22 of aluminium, and 1 of charcoal. *Cheddite* is another explosive of this general class, known in various forms as a blasting explosive; the chief constituent is potassium chlorate (up to about 80 per cent.), with nitronaphthalene, castor oil, and other nitro-hydrocarbons as subsidiary ingredients.

"Permitted" explosives for use in "fiery" coal-mines (p. 60) often contain ammonium nitrate as the chief constituent, and the average percentage compositions of some typical examples of such

explosives may be quoted in illustration: *Ammonite*, ammonium nitrate 73, sodium chloride 21, dinitronaphthalene 5, moisture 1; *Bellite No. 1*, ammonium nitrate 63, sodium chloride 16, trinitrotoluene 15, starch 4, moisture 2; *Tees Powder*, ammonium nitrate 60, sodium chloride 20, nitro-glycerine 10, wood meal 9, moisture 1.

A particularly interesting series of explosives, which must be regarded as modified gunpowders, have been elaborated as a consequence of the commercial production of liquefied air in 1895: these are known as *liquid oxygen explosives*, or *LOX*. In them, liquid oxygen replaces potassium nitrate, sulphur is omitted, and carbon is supplied as lampblack, cork dust, wood pulp, or sometimes in the form of hydrocarbons absorbed in inert porous materials. Since the individual constituents are non-explosive and mixed just before use, these explosives belong to the Sprengel type of "safe" explosives (p. 120).

As liquid oxygen boils at the extremely low temperature of −183° C., it has to be kept in double-walled vacuum-insulated vessels of the Dewar, or "thermos" type. The carbonaceous material, contained in porous paper or cloth cartridges, is soaked in the oxygen and used soon after removal, being fired with a suitable detonator. Some LOX explosives are equal to dynamite in power; the detonation velocity varies from about 3000 to 6000 metres per second.

The dipped cartridges lose their absorbed oxygen rapidly when removed from their very cold bath. A lampblack cartridge keeps its maximum power for a few minutes only, but the effective life of a large cartridge may last for several hours. There is danger in using partly spent LOX cartridges in underground workings, owing to the formation of poisonous carbon monoxide, and even fresh cartridges of this kind must not be used in coal-mines because of danger from the oxygen in presence of firedamp and dust. LOX explosives have several advantages: they are often cheaper than dynamite, they may be used in the coldest climates, they become innocuous on exposure, and they do not need to be stored in magazines.

Explosives of this kind were first used on a large scale in blasting operations during the construction of the Simplon

Tunnel in 1899. In recent years the annual consumption of liquid oxygen for making blasting explosives in Germany alone has exceeded a million litres.

Altogether, these novel agents form an intriguing addition to the long explosive train of gunpowder and its derivatives extending from the bare monastic cell of Roger Bacon through some seven centuries to the complex laboratories and factories of the present day.

CHAPTER VII

THE COMING OF MODERN EXPLOSIVES

GUNPOWDER was discovered in the alchemical period, more than five hundred years before the dayspring of scientific chemistry. One of the harbingers of that dawn, which heralded the opening of the nineteenth century, was a great Swedish chemist named Scheele. He was a struggling apothecary, "always tormented by material wants", and yet in the course of his short life (1742–1786) he made many first-class contributions to experimental chemistry, of which he wrote in his enthusiasm: "You may think perhaps that material cares are going to absorb me, and take me away from experimental chemistry. Not so! That noble science is my ideal."

Among Scheele's discoveries was that of a substance which became known later as glycerine, or glycerol. Between the years 1779 and 1783 Scheele found that this sweet, syrupy liquid could be obtained by heating various fixed oils of plant or animal origin, such as olive oil, linseed oil, rape-seed oil, almond oil, hog's lard, and butter, with litharge and water. Later, between 1811 and 1823, Chevreul, a French chemist who lived to be a centenarian (1786-1889), showed that these natural fats and oils in general could be broken down into a mixture of "Scheele's sweet principle" and a variety of organic acids, composed largely of the so-called fatty acids. Scheele's sweet, bland liquid, which became known as a pleasant remedy for chapped skin, was destined in the fullness of time to become a substance of the first importance in the manufacture of modern explosives; but not until gunpowder had reigned supreme for a period of six centuries.

Now glycerine is an organic substance. Organic chemistry began to take shape as a definite branch of science about 1830, but it was not until 1858 that its fundamental theory of molecular structure was put forward by Kekulé and Couper (p. 28). These dates are significant, because a command of organic chemistry was essential before an organic explosive could be prepared and applied. It was in 1846 that an Italian chemist, Sobrero, first prepared **nitro-glycerine** by nitrating glycerine, and in 1863

that the Swedish chemist and engineer, Nobel, began to apply it as a blasting explosive. "Nobel's blasting oil", as it was called, was very dangerous to handle owing to the capricious occurrence and great violence of its explosion; but with Nobel's invention of **dynamite** (1866), followed by that of the still more powerful **blasting gelatine** (1875), this difficulty was overcome (p. 97), and at the present day nitro-glycerine enters into the composition of a large number of explosives of different types.

Meanwhile, developments of an organic chemical nature were occurring in another direction. In 1838, Pelouze obtained a highly-inflammable material by treating cotton with strong nitric acid, and thereby opened the way to the study of materials which became known as **nitro-celluloses.** Schönbein improved this process in 1845 by using a mixture of nitric and sulphuric acids for the nitration of cotton, and characterised the product, in 1846, as a new explosive far exceeding gunpowder in its power. It was not until 1865, however, that the practical difficulties of applying this so-called **guncotton** as a shattering explosive were overcome, mainly through the work of Sir Frederick Abel.

Thus, in 1865, gunpowder's age-long position as a blasting explosive had been undermined from two directions. Concurrently, attempts were being made to utilise nitrated cellulose as a propellant by reducing its rate of combustion. Various cooling agents and inert materials were added, but the best results followed the application of gelatinising solvents. It was not until 1886, however, that a really satisfactory propellant of this type was obtained by Vieille; this was a horn-like product made by treating a suitably nitrated cellulose (p. 111) with a mixture of alcohol and ether. This early type of **smokeless powder** was used in the Lebel rifle by the French under the name of "Poudre B", after General Boulanger.

It was left to the genius of Nobel to unite the two lines of research starting from glycerine and cotton, and to show that the explosive properties of nitrated cotton could be tamed for propellent purposes by gelatinising the fibrous material with nitro-glycerine. This discovery, that the two most powerful explosives then known could be blended to furnish a slow-burning propellant, "was so startling that it was received with

incredulity, which soon gave place to extreme astonishment." The resulting smokeless powder, known as **ballistite,** was patented in 1888. Nobel claimed that this patent was infringed through the production of **cordite** by Sir Frederick Abel and Sir James Dewar, in 1889–1890, but the ensuing lawsuits ended in favour of the British Government.

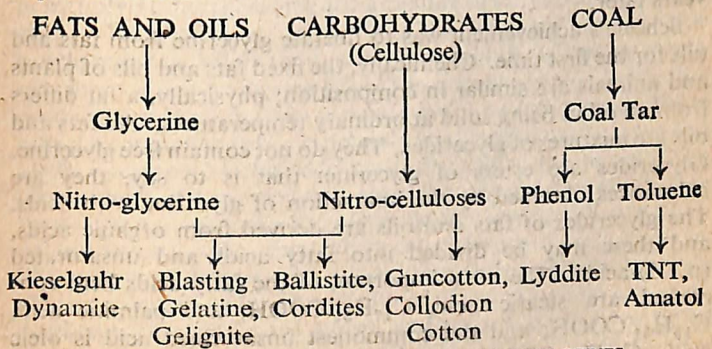
Alfred Bernard Nobel (1833–1896) is the outstanding figure in the history of explosives. Unlike his fellow-countryman, Scheele, he was not tormented by material wants; on the contrary, his invention of dynamite and other explosives, and his general energy and enterprise, enabled him to amass an enormous fortune. Describing his method of elaborating an invention, he once said: "I worked intermittently; I left it off and then I returned to it. It is very much my way of doing, but I always return to the same thing, having the idea that I must ultimately succeed." In Great Britain alone he took out 122 patents. Of primary importance was his invention, in 1864, of the **detonator,** whereby the explosion of a small charge of gunpowder or mercury fulminate was used to bring about the detonation of the main explosive (p. 59). Without this discovery and application of sympathetic detonation it would have been impossible to unlock effectively the highly-concentrated energy of modern explosives. At his death, Nobel left the bulk of his fortune in trust for the foundation of Nobel Prizes for physics, chemistry, medicine, literature—and peace. When a suitable recipient cannot be found for a particular Prize in one of the annual periods, the Prize is reserved. Of all these Nobel Prizes, the Peace Prize has been reserved most frequently.

Explosives originating from fats and carbohydrates were soon supplemented by **coal-tar explosives,** originating ultimately from coal. The inception of the great coal-tar chemical industries may be traced back to the preparation of the first synthetic dye from coal-tar aniline by Sir William Perkin, in 1856. This spectacular discovery led to the gradual recognition during the last half of the nineteenth century that coal tar was a potential source of an enormous number of dyes, perfumes, medicinal and photographic chemicals, and other useful kinds of organic compounds. These do not occur ready-made in the tar. The

"primaries" actually found in the tar (benzene, toluene, phenol, naphthalene, etc.) are converted by chemical treatment into "intermediates" (nitrobenzene, aniline, benzaldehyde, etc.), and these in turn are used in the synthesis of the finished dyes and other fine chemicals by the application of further chemical processes.

Among the fine chemicals produced in this way are many with explosive properties. The first of these to be recognised as an effective explosive was picric acid, obtained from phenol (carbolic acid) by nitration. Sprengel showed, in 1871, that picric acid could be detonated with mercury fulminate; later, in 1885, Turpin introduced it as a filling for shells, and it was used as a high explosive under the names of **lyddite,** melinite, shimose, etc. Since that time **trinitrotoluene** (TNT) and a considerable variety of other substances prepared from coal tar have been used as explosives.

To sum up: the concurrent exploitation of fats and carbohydrates, represented particularly by glycerine and cotton, as sources of explosives was soon followed by the utilisation of coal tar to the same end. Glycerine, cotton and coal tar are, indeed, the three main pillars of the modern explosives industry. A selection of the most important explosives derived from each of these sources, taken in the above order, will now be considered. The subjoined diagram summarises some of the fundamental relationships concerned:



ANCESTRY OF SOME TYPICAL MODERN EXPLOSIVES

CHAPTER VIII

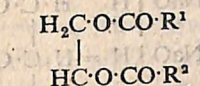
FROM FATS TO DYNAMITES

Fats to Glycerine

"LET me have men about me that are fat: sleek-headed men and such as sleep o' nights." These sentiments, attributed by Shakespeare to Caesar, reflects the popular idea that an accumulation of fat in the human body leads to good temper, lethargy and somnolence. Dickens embroidered the same theme in *Pickwick Papers*: "The fat boy laid himself affectionately down by the side of the cod-fish: and placing an oyster-barrel under his head for a pillow, fell asleep instantaneously." In the light of this popular idea it is interesting to find that the fats are decidedly inert and lethargic from the chemical point of view. Yet, as we have already seen (p. 47), they possess a great store of latent energy. They may be regarded, indeed, as the sleeping dogs of organic chemistry. Their age-old slumbers were first disturbed by Scheele in 1779, but they did not begin to bark until they received a more violent stimulus from a second Swede nearly a hundred years later.

Scheele's achievement was to liberate glycerine from fats and oils for the first time. Chemically, the fixed fats and oils of plants and animals are similar in composition; physically, a fat differs from an oil in being solid at ordinary temperatures. All fats and oils are mixtures of glycerides. They do not contain free glycerine. Glycerides are esters of glycerine: that is to say, they are substances obtained by the interaction of glycerine with acids. The glycerides of fats and oils are derived from organic acids, and these may be divided into fatty acids and unsaturated (p. 25) acids. The most important of the fatty acids here concerned are stearic acid, $C_{17}H_{35}.COOH$, and palmitic acid, $C_{15}H_{31}.COOH$; and the commonest unsaturated acid is oleic acid, $C_{17}H_{33}.COOH$, which lacks two hydrogen atoms per

molecule as compared with the saturated stearic acid. The first two of these acids are crystalline solids, and oleic acid is an oily liquid. Oleic acid is furnished in greater amount by oils than by fats. All of the numerous glycerides found in these natural fats and oils may be represented by the following general formula, in which the univalent radical R may be $C_{17}H_{35}$ (of stearic acid), $C_{15}H_{31}$ (of palmitic acid), $C_{17}H_{33}$ (of oleic acid), and many others:

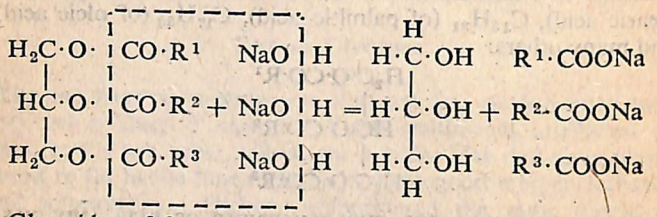


GENERAL FORMULA FOR THE GLYCERIDES OF FATS AND OILS

The radical R may be provided by a very large number of fatty or unsaturated acids, and in a specific glyceride the three R's may be alike or different. When it is added that any particular natural fat or oil is a mixture of such glycerides, the great variety of these natural materials is accounted for.

When fats or oils are treated with hot dilute mineral acids, or with superheated steam in presence of small amounts of certain metallic oxides as catalysts or promoters, they are broken down, or hydrolysed, into glycerine and a mixture of fatty and unsaturated acids. The solid acids are used in the form of "stearine" for candle-making. When the hydrolysis is brought about by means of dilute sodium hydroxide ("lye") in a steam-heated kettle, the products are glycerine and the sodium salts of the acids. These salts are soaps, and they are precipitated ("salted out") at the end of the operation by the addition of dry salt to the liquor. The filtrate from the precipitated soap, known as "spent lye" or "sweet water", contains the glycerine in solution. From it, by neutralisation and other chemical treatment, followed by filtration and evaporation under diminished pressure, crude glycerine is obtained. This is filtered through animal charcoal, distilled with superheated steam, and then fractionally distilled in steam-heated vacuum-pans under diminished pressure. For

cosmetic and certain other purposes the glycerine must be perfectly colourless ("water-white"), but a pale yellow or brownish tint is permissible in "dynamite glycerine". The general scheme for the hydrolysis, or saponification (p. 46), of fats and oils is depicted below:


H2C·O· CO·R1 NaO H H H·C·OH R1·COONa
HC·O· CO·R2 + NaO H = H·C·OH + R2·COONa
H2C·O· CO·R3 NaO H H·C·OH R3·COONa
H
Glycerides of fats and oils.
Alkali.
Glycerine.
Hard soap.

The manufacture of glycerine is thus inseparably bound up with the important soap-making and candle-making industries, in both of which glycerine is a valuable by-product. From what has been said, it is evident that the application of glycerine in the manufacture of explosives does not interfere with the use of fats and oils in these industries. On the other hand, when the fats and oils have been broken down in this way they are no longer useful as foodstuffs.

Since it possesses the repeated –CH(OH)– grouping characteristic of carbohydrates, glycerine may be looked upon as a carbohydrate fragment which serves as a kind of "molecular trident" in holding together the structures of fats and oils. From this point of view it is interesting that a small amount of glycerine is a normal product in the alcoholic fermentation of sugars. By adding sodium sulphite to the fermenting liquid it is said that the yield may be increased to 20 per cent. or more: owing to the shortage of fats during the war of 1914-1918, glycerine was at that time produced industrially in Germany from sugar by this method.

Glycerine is a colourless syrupy liquid; it has a sweet taste, and is miscible with water. It boils at 290° with slight decomposition,

and for this reason is purified at a lower temperature, by distillation under diminished pressure. Chemically it is a trihydric alcohol: that is to say, it has three alcohol groups (–OH) in the molecule—these being the "prongs" of the "trident". The name glycerol, with the suffix *-ol* indicating an alcohol, is therefore preferable to the popular name, glycerine.

Glycerine to Nitro-glycerine

Alcohols react with acids to form esters, and one molecule of the trihydric alcohol, glycerol, requires three molecules of a monobasic acid for complete esterification. Esterification is the reverse of saponification or hydrolysis, and Berthelot showed in 1854 that simple synthetic fats could be prepared by heating mixtures of glycerine and fatty acids to about 300° in sealed tubes.

The nitration of glycerine is an essentially similar process, in which the fatty acids are replaced by nitric acid, applied in the presence of sulphuric acid at ordinary temperatures. The resulting oily compound, commonly known as "nitro-glycerine", is thus an ester of glycerol with nitric acid: "nitro-glycerine" is a misnomer, as the substance is in reality glyceryl trinitrate, and not a true nitro-compound (p. 52). *Nitro*-glyceri*ne* is therefore doubly misnamed.

The function of sulphuric acid in the nitration of glycerine, shown by the appended structural formulæ, is to facilitate the elimination of the water which is formed in the process:

$$\begin{array}{l} H_2C\cdot O\,|\,H \quad HO\,|\cdot NO_2 \\ \quad\;|\quad\;|\quad\;| \\ HC\cdot O\,|\,H + HO\,|\cdot NO_2 \\ \quad\;|\quad\;|\quad\;| \\ H_2C\cdot O\,|\,H \quad HO\,|\cdot NO_2 \end{array} = \begin{array}{l} H_2C\cdot O\cdot NO_2 \\ \quad\;| \\ HC\cdot O\cdot NO_2 + 3H_2O \\ \quad\;| \\ H_2C\cdot O\cdot NO_2 \end{array}$$

Glycerine. Nitric acid. Nitro-glycerine. Water.

In this typical ester of nitric acid, or alcohol nitrate, the nitro-group is attached directly to oxygen, as part of a nitrate group, $-NO_3$, and not to carbon as in true nitro-compounds. The

arrival in the molecule of these nitro-groups, or molecular fifth columnists, heralds the birth of an explosive substance from a bland progenitor, glycerine, derived in turn from the placid fats and oils. The molecular dogs have been at last aroused from their slumbers, and are straining "like greyhounds in the slips", ready to bark and scatter in all directions.

Nobel was the pioneer in the commercial manufacture of nitro-glycerine. In principle, the manufacture is simple, but from time to time various modifications have been made in the apparatus and procedure, in the interests of safety and convenience. The strictest precautions are necessary in making and handling this substance, which is one of the most powerful and most dangerous of all explosives. Its preparation should not be attempted in an ordinary laboratory. In technical practice it is usual to conduct all dangerous operations in the manufacture of explosives in segregated buildings screened by mounds.

One of the most efficient methods of manufacture utilises a nitrator-separator patented in 1901 by Nathan, Thomson and Rintoul, a form of which is shown diagrammatically in Fig. 7. This has the advantage of allowing the operations of nitration and separation to be carried out in one apparatus; moreover, it dispenses with the earthenware cocks which have sometimes proved a source of trouble in other forms of apparatus. The nitrator-separator is a cylindrical leaden vessel, with a sloping bottom and a conical roof provided with observation windows and carrying a thermometer which acts as a guide to the operator.

The nitrating acid is admitted through a pipe connected with the lowest part of the apparatus; it is then brought to a temperature of about 16° by means of coils through which water or brine is circulated. A suitable acid may contain, for example, about 41 per cent. of nitric acid, 57·5 per cent. of sulphuric acid, and 1·5 per cent. of water; a somewhat stronger acid, containing only about 0·5 per cent. of water, is sometimes used, in the proportion of 620 parts of nitrating acid to 100 parts of glycerine, the yield of nitro-glycerine being then about 230 parts.

The glycerine, owing to its viscosity, is thinned by being warmed to about 30°, before being admitted gradually into the nitrating acid. The liquid is kept in constant agitation by the

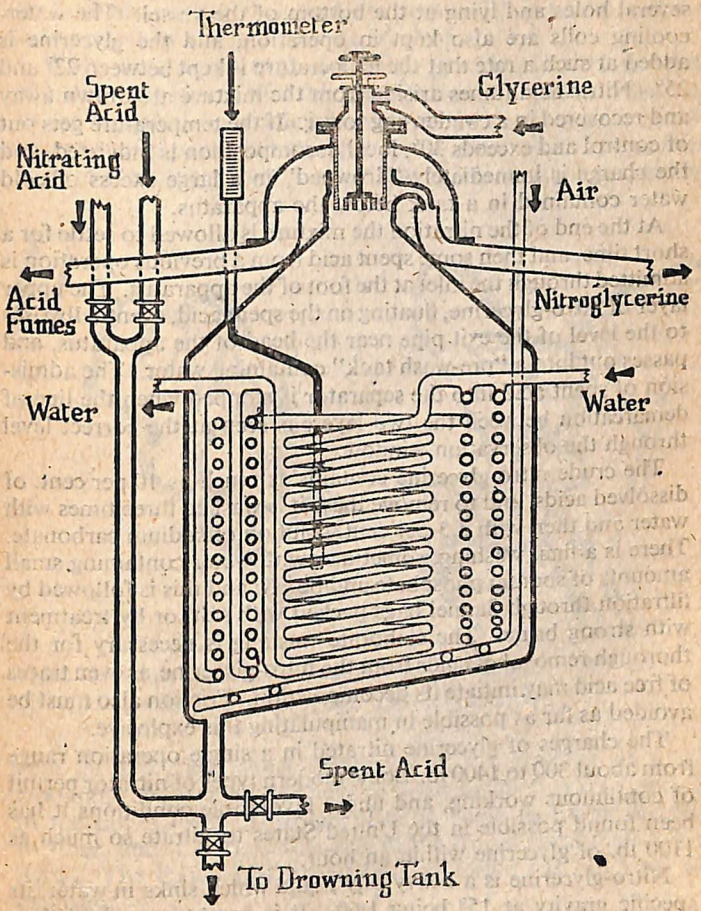


FIG. 7.—THE NITRATOR-SEPARATOR

introduction of compressed air through a coil provided with several holes and lying at the bottom of the vessel. The water-cooling coils are also kept in operation, and the glycerine is added at such a rate that the temperature is kept between 22° and 25°. Nitric acid fumes arising from the mixture are drawn away and recovered in a condensing tower. If the temperature gets out of control and exceeds 30°, local decomposition is indicated, and the charge is immediately "drowned" in a large excess of cold water contained in a tank below the apparatus.

At the end of the nitration the mixture is allowed to settle for a short time, and then some spent acid from a previous operation is admitted through the inlet at the foot of the apparatus. The upper layer of nitro-glycerine, floating on the spent acid, eventually rises to the level of the exit pipe near the head of the apparatus, and passes out into a "pre-wash tank" containing water. The admission of spent acid into the separator is stopped when the line of demarcation between the two layers is seen at the correct level through the observation window.

The crude nitro-glycerine contains as much as 10 per cent. of dissolved acids, and to remove these it is washed three times with water and then with a 3 per cent. solution of sodium carbonate. There is a final washing, sometimes with water containing small amounts of sodium phosphate and borax; and this is followed by filtration through flannel bags packed with salt, or by treatment with strong brine. The elaborate washing is necessary for the thorough removal of acids from the nitro-glycerine, as even traces of free acid may initiate its decomposition. Friction also must be avoided as far as possible in manipulating this explosive.

The charges of glycerine nitrated in a single operation range from about 300 to 1400 lb. Some modern types of nitrator permit of continuous working, and under favourable conditions it has been found possible in the United States to nitrate so much as 1100 lb. of glycerine within an hour.

Nitro-glycerine is a heavy oily liquid which sinks in water, its specific gravity at 15° being 1·60. It is much more fluid than glycerine, and when pure is colourless and odourless. It has a pronounced physiological action, continued exposure to its vapour leading to drowsiness and the so-called "NG headache":

immunity is usually attained after a few days, and relief is afforded by fresh air, aspirin, or morphine. Susceptibility to these effects is increased by the habitual use of alcohol.

When used as an explosive, nitro-glycerine is often denoted shortly by the letters NG; this use of letters is a common practice in the technical nomenclature of explosives, although it is not acceptable for purely scientific purposes. The explosive properties of nitro-glycerine are very marked, but as it is readily detonated by

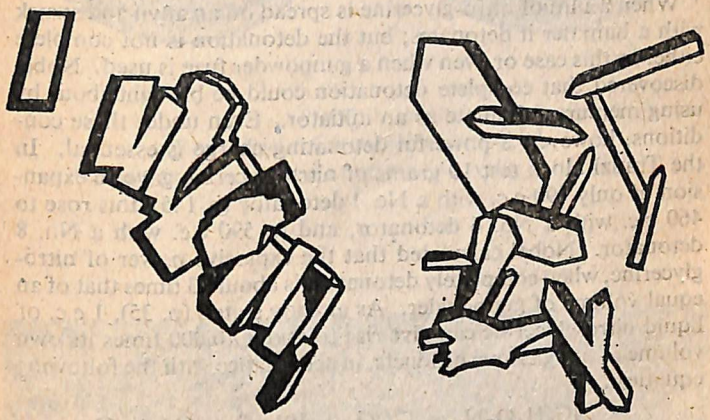


FIG. 8.—THE TWO FORMS OF NITRO-GLYCERINE CRYSTALS (m.p. 2° and 13·2°) (After Ullmann)

heat (at 180°) and shock, especially in the presence of small amounts of impurities, it cannot be safely handled or transported in the liquid form. Nitro-glycerine is liable to freeze in cold weather, and it is more sensitive in the frozen form than when liquid. The thawing of frozen nitro-glycerine has often led to explosions.

It has been found that nitro-glycerine gives rise to two solid crystalline forms (Fig. 8): one of these consists of labile rhombic leaflets, m.p. 2°, the other of hard prismatic needles, m.p. 13·2°.

Rubbing or shock is sufficient to bring about a transformation of the labile rhombic form into the stable prismatic form; the change is accompanied by the liberation of 28 calories of heat per gram, and it is possible that this exothermic transformation has been the cause of a number of unexplained explosions of nitro-glycerine. It may be remarked in this place that any property of a substance with industrial applications repays careful study, as however abstruse the property may appear it may lead to important and unexpected consequences.

When a film of nitro-glycerine is spread on an anvil and struck with a hammer it detonates; but the detonation is not complete either in this case or even when a gunpowder fuze is used. Nobel discovered that complete detonation could be brought about by using mercury fulminate as an initiator. Even under these conditions, however, a powerful detonating charge is essential. In the Trauzl block test 10 grams of nitro-glycerine gave an expansion of only 190 c.c. with a No. 1 detonator (p. 145); this rose to 460 c.c. with a No. 6 detonator, and to 590 c.c. with a No. 8 detonator. Nobel calculated that the explosive power of nitro-glycerine, when completely detonated, is about 13 times that of an equal volume of gunpowder. As already stated (p. 35), 1 c.c. of liquid nitro-glycerine can give rise to about 10,000 times its own volume of hot gaseous products, in accordance with the following equation:

$$4C_3H_5O_9N_3 = 12CO_2 + 10H_2O + 6N_2 + O_2.$$

Much frozen nitro-glycerine was safely transported from the Hoosac Tunnel works, in the United States; but in modern practice, nitro-glycerine is never used alone as an explosive, owing to its dangerously capricious properties. It is manufactured on a very large scale for use in making dynamites, gelatines and smokeless powders.

Certain other alcohol nitrates have been applied to some extent as explosives. Among these are **nitroglycol, diglycerine tetranitrate** and **penthrit.** The first two of these are liquids, used sometimes in admixture with nitro-glycerine in the manufacture of non-freezing dynamites. Glycol, $CH_2(OH)\cdot CH_2(OH)$, is the dihydric analogue of glycerol; it may be made from ordinary

PLATE 1 (A).

Roger Bacon Commemorative Medal.
(By Gayrard, in Durand's numismatic series, Paris, 1818.)

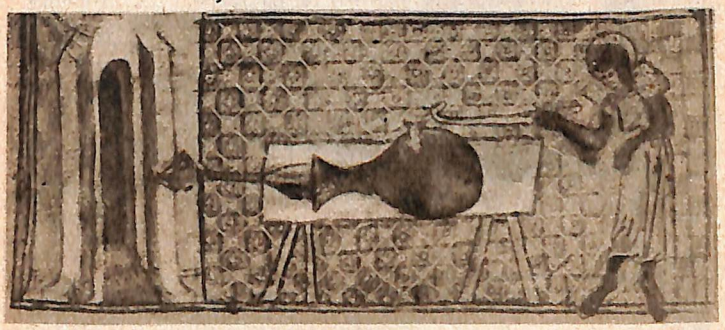


PLATE 1 (B).

The Oldest Gun, 1325.
(From *De officiis regum* by Walter de Millemete, in the library of Christ Church, Oxford.)

PLATE 2.

A Primitive Filter Press for Saltpetre.
(From a 15th-century MS. in the Vienna I.R. Court Museum.)

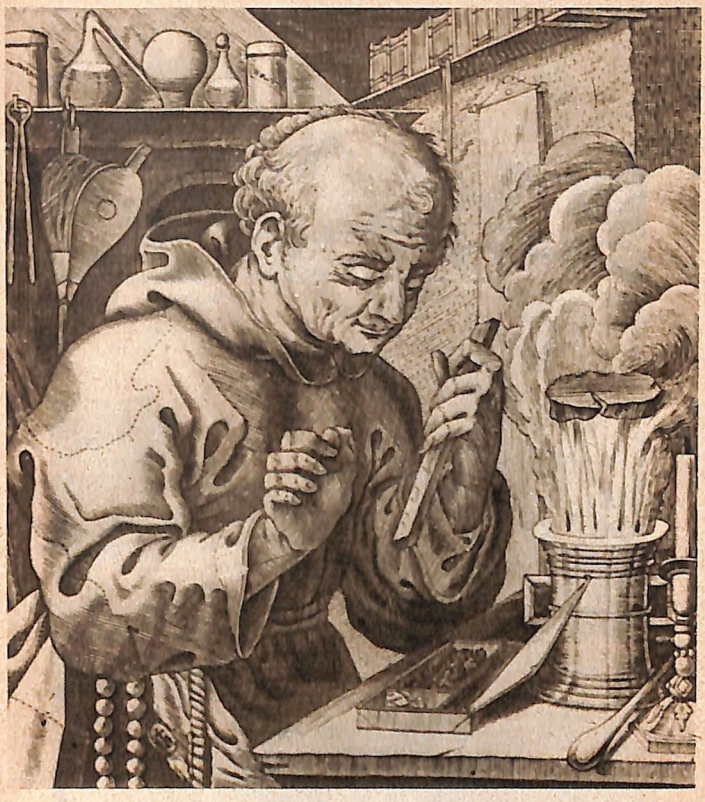
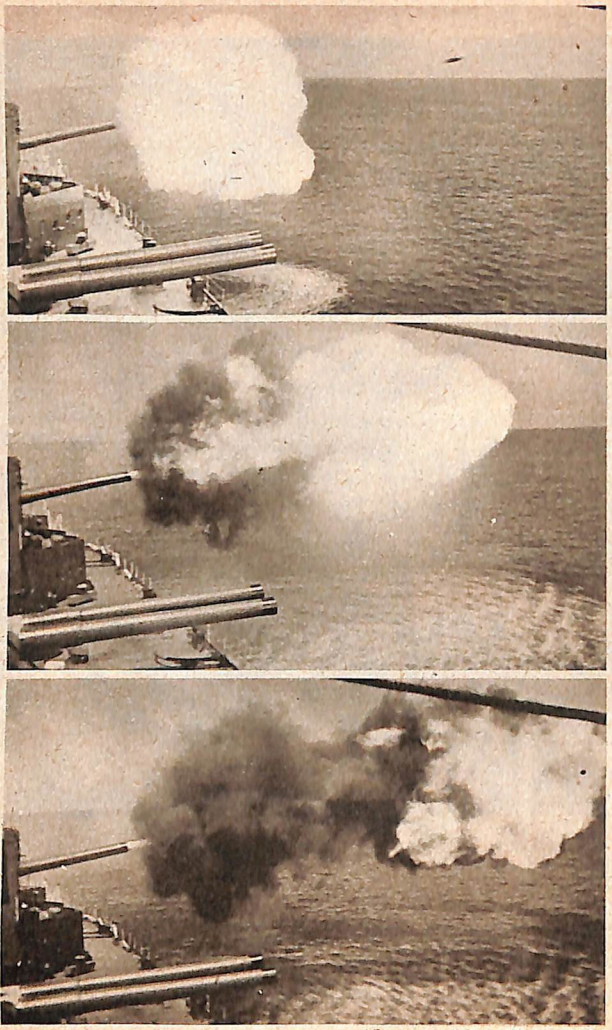


PLATE 3.

Berthold Schwarz in his Laboratory.
(From a copper engraving by R. Custos, 1643.)



(*Courtesy of Fox Photos, Ltd.*)

PLATE 4.

Firing a British Naval Gun.

Showing successive phases in the expansion of gases and smoke and in the vibratory disturbance in the sea.

PLATE 5.

Quayle Spark Photographs.

1. Leakage of explosion gases in advance of the bullet.
2. Bullet enveloped in explosion gases.
3. Bullet 11 inches from muzzle, with individual air-wave (*see* p. 142).

(From *The Encyclopædia Britannica*, 14th ed., 1929.)

(British Official Photograph.)

PLATE 6.
Making up Cordite Charges.

(*British Official Photograph.*)

PLATE 7.

Fitting Shells with Exploders.

(British Official Photograph.)

PLATE 8.

Assembling Fuzes.

ethyl alcohol via ethylene, and when nitrated it yields nitroglycol, otherwise glycol dinitrate, $(CH_2 \cdot O \cdot NO_2)_2$. Diglycerine, $(CH_2OH \cdot CHOH \cdot CH_2)_2O$, is prepared from glycerine by heat treatment and nitrated in the same way as the parent compound. Penthrit, $C(CH_2 \cdot O \cdot NO_2)_4$, is a solid explosive which has been found useful in certain kinds of detonators.

Nitro-glycerine to Dynamites

Nobel began to manufacture nitro-glycerine on a large scale in a factory near Stockholm in 1863, but during the next few years so many accidents attended its manufacture, transport and use as a blasting explosive that in some countries, including Great Britain, it was prohibited. Nobel found that when dissolved in wood spirit it could be transported safely, but the recovery of the nitro-glycerine by precipitation with water was a very troublesome process. Apart from this, as a liquid explosive, nitro-glycerine was liable to be dangerous in blasting operations, owing to its tendency to creep into cracks and fissures in the rock and remain unexploded.

Nothing daunted, the indomitable Nobel then turned to possible solid absorbents. Gunpowder, charcoal, and other materials were tried with little success; but eventually he discovered an excellent absorbent in a curious infusorial earth known as kieselguhr, or diatomite. This is a white earth, soft and porous, found in Germany, Scotland, California, Canada, and other parts of the world; it consists of the siliceous skeletons of minute aquatic plants called diatoms, and has a great absorbent capacity. Dried kieselguhr is able to absorb three or four times its weight of nitro-glycerine. Nobel named the mixture **dynamite** (Greek, *dynamis*, power), and patented the process in 1867. Originally he had intended merely to transport the nitro-glycerine in the safe form of dynamite, leaving it to be extracted and used in the liquid form on the site. He was therefore agreeably surprised to find that dynamite could be detonated more readily than raw nitro-glycerine: thus, dynamite came into use as a new and very convenient blasting explosive.

Ordinary dynamite is a mechanical mixture of nitro-glycerine,

a liquid explosive substance, with kieselguhr, a solid material composed mainly of silica. This first dynamite to be prepared is now known as Kieselguhr Dynamite, Guhr Dynamite, or Dynamite No. 1. It was the precursor of many other fundamentally similar compositions, in all of which a solid material, called the *base* or *dope*, is used to absorb and retain the liquid nitro-glycerine under ordinary conditions of storage. These materials are all embraced under the generic name of **dynamites**.

Dynamites may be classified under three heads, as dynamites with an **inert base**, a **combustible base**, or an **explosive base**. In the first type the explosive energy is derived wholly from the nitro-glycerine; but in the second and third types a contribution is made by the base, which is able at the same time to utilise the slight excess of oxygen contained in the nitro-glycerine (p. 54). The proportion of nitro-glycerine in dynamites is limited by their tendency to exude the oily substance when stored. The stability of nitro-glycerine is lessened markedly by traces of acid to which it may give rise on storage, and small amounts of calcium or magnesium carbonate are often incorporated in dynamites to improve their keeping qualities by neutralising acid impurities.

Inert-base Dynamites

Kieselguhr Dynamite, or *Dynamite No. 1*, is the best-known dynamite with an inert base, and it is usually composed of about 75 parts of nitro-glycerine to 25 parts of kieselguhr. The ingredients are thoroughly incorporated by hand-kneading in shallow leaden tanks, the nitro-glycerine being poured on to the guhr from a rubber bucket. The plastic material is then broken into grains by rubbing it through a sieve, and these are finally squeezed from a cartridge machine into cylindrical cartridges somewhat less than an inch in diameter. The cartridges are protected by a wrapping of waterproofed paper.

Kieselguhr dynamite is a plastic grey paste, which is sometimes coloured orange, pink or brown by ochre. Its specific gravity is about the same as that of nitro-glycerine (1·6). Small quantities of dynamite, when ignited, burn quickly without

exploding; but large quantities burn to detonation. Dynamite, if unfrozen, may be ignited safely and destroyed by spreading it into a train and soaking it with paraffin oil. When struck on an anvil, only those parts of the dynamite coming into contact with the hammer undergo detonation.

Dynamite freezes at about 4° C., and frozen dynamite is liable to explode upon ignition. This readiness to freeze is one of the chief drawbacks of ordinary dynamite, since it does not detonate properly when frozen; thawing has to be carried out carefully in pans with warm-water jackets. The freezing temperatures of dynamites for use in cold climates may be lowered considerably by using nitro-glycerine containing some nitro-glycol or di-glycerine tetranitrate.

Dynamite is much less sensitive to shock than nitro-glycerine, but it is readily detonated by the shock of a rifle bullet. Dynamite is fired by embedding in it a mercury fulminate detonator of sufficient strength, this being set off either electrically or by means of a safety fuze (p. 145). A standard detonator used for this purpose contains 0·5 g. of a mixture of 70 per cent. of mercury fulminate with 30 per cent. of potassium chlorate ($KClO_3$). The rate of detonation is about 6100 metres per second. Dynamite is about three times as powerful as gunpowder; in a Trauzl block test (p. 64) its relative power was found to be 0·71, in comparison with nitro-glycerine as unity.

Kieselguhr dynamite is an explosive of high *brisance*, and its effect is so localised and shattering as to render it unsuitable for many mining operations. Its power cannot be conveniently moderated by decreasing the proportion of nitro-glycerine, owing to the increasing difficulties of detonation, which cannot be brought about at all if less than 30 per cent. of nitro-glycerine is present. It is on this account that modified dynamites with an explosive base have displaced kieselguhr dynamite in mining practice. Another disadvantage of guhr dynamite is that it cannot be used in contact with water, as under these conditions it separates into its constituents. Stored dynamite should be kept dry at temperatures above its freezing-point and out of direct sunshine.

Mica powder may be quoted as another example of a dynamite

with an inert base, which in this case consists of fine scales of mica.

Combustible-base Dynamites

Carbodynamite is an example of a dynamite with a combustible base, the absorbent being cork charcoal: this constitutes only about 10 per cent. of the explosive, the remainder being nitro-glycerine. Carbodynamite is thus much more powerful than kieselguhr dynamite. In *Grisoutite*, another explosive of this class, the absorbent is wood meal, and some magnesium sulphate is added.

Explosive-base Dynamites

Dynamites with an explosive base form an important, varied, and numerous group. A large number of them contain highly-oxygenated inorganic salts as the base. For example, *Dynamite No. 2* contains about 58 per cent. of nitre and up to 18 per cent. of nitro-glycerine, with smaller amounts of charcoal and other constituents. *Atlas Powders* may contain from about 20 to 75 per cent. of nitro-glycerine, with sodium or potassium nitrates, wood pulp or sawdust, and a little magnesia or chalk; *Hercules Powders* are closely similar to Atlas Powders. *Lithofracteur* is composed chiefly of nitro-glycerine, kieselguhr and charcoal (or powdered coal, bran or sawdust), with smaller quantities of sodium or barium nitrates, sulphur, and manganese dioxide. *Ammonia dynamites* may contain as much as 85 per cent. of ammonium nitrate, with about 10 per cent. of nitro-glycerine, the remainder being charcoal or wood meal. *Dynobel* contains about 33 per cent. of nitro-glycerine, 28 per cent. each of potassium perchlorate ($KClO_4$) and ammonium oxalate, the remainder being wood meal with not more than 1 per cent. of collodion cotton.

The most widely-used explosives of this class contain nitrated cellulose (nitro-celluloses) as the explosive base. Their introduction was due to Nobel, as a result of experiments directed towards the production of a non-exuding dynamite. He had tried guncotton as a base without success in 1867, soon

after his original invention of dynamite. A less highly nitrated cotton, known as collodion cotton (p. 110), is sometimes used in ether-alcohol solution under the name of "newskin" for depositing a protective film over a cut, and it is said that a cut finger led Nobel, in 1875, to try the effect of mixing nitro-glycerine and collodion cotton in presence of a solvent. The result was the solution of his problem and the birth of *Blasting Gelatine.*

The usual blend for blasting gelatine consists of 7 per cent. of collodion cotton and 93 per cent. of nitro-glycerine. The slight excess of oxygen in the nitro-glycerine counterbalances a deficit in the collodion cotton, and the result is an explosive of very high power, unrivalled for blasting hard rock. Blasting gelatine is a light-yellow solid, translucent and elastic, with the same specific gravity as kieselguhr dynamite and nitro-glycerine (1·6). It has the great advantage of being unaffected by water. When heated to 200° C. it explodes, but small quantities may be ignited and burnt in the open without detonation. It freezes at about 2° to 4° C. and then becomes more sensitive to shock: in its frozen state only, it may be exploded by the impact of a rifle bullet. Frozen cartridges of blasting gelatine have to be thawed with care, like those of guhr dynamite.

Blasting gelatine is harder to detonate than guhr dynamite, and in working practice it needs a detonator containing not less than 1 gram of cap composition; sometimes a guhr dynamite gaine or "booster" is used (p. 60). The velocity of detonation then attains 6800 metres per second, and the power as determined by the Trauzl test is 1·6 times that of guhr dynamite.

For the manufacture of blasting gelatine it is essential to use a carefully prepared and dried collodion cotton with a high nitrogen content. There is no need to use a solvent in the incorporation, the collodion cotton being stirred gradually, with the aid of a wooden paddle, into the nitro-glycerine; this is maintained at 35° to 40° in a copper or leaden trough surrounded by a hot-water jacket. In about 2 hours the mixture is completely transformed into a semi-transparent jelly, which is then worked awhile by hand, or by a mechanical kneading machine. The warm paste is finally worked into cylindrical cartridges in a

suitable machine, and these are wrapped in a waterproofed paper. Sometimes a little chalk, magnesium carbonate, or vaseline is added to the gelatine as a stabiliser.

Milder explosives of the same type are manufactured by using relatively less collodion cotton and kneading the resulting thinner jelly with absorbing powders containing nitre, wood meal, and other ingredients. *Gelatine Dynamite* and *Gelignite* are two of the most valuable explosives of this kind. The appended table shows the composition and relative explosive power of the three most important dynamites of this type, together with the corresponding data for kieselguhr dynamite:

	Kieselguhr Dynamite	*Blasting Gelatine*	*Gelatine Dynamite*	*Gelignite*
Nitro-glycerine ..	75	93	63·4	60
Collodion cotton ..	—	7	1·6	5
Potassium nitrate ..	—	—	26·25	27
Wood meal.. ..	—	—	8·4	8
Sodium carbonate..	—	—	0.35	—
Kieselguhr	25	—	—	—
Power .. .. (Trauzl test)	100	160	125	100

COMPOSITIONS OF SOME DYNAMITES

There are many other explosives of this general type, as for example, *Ammonia Gelignite* (containing ammonium nitrate, NH_4NO_3), *Duxite*, *Essex Powder*, *Rippite*, *Saxonite* and *Samsonite*.

The numerous "straight dynamites" based upon nitro-glycerine possess the common drawback of freezing in cold weather. This may be prevented either by warm storage or by adding to the explosive a constituent which lowers the freezing-point of the nitro-glycerine. Low-freezing dynamites have been produced in the United States, especially, as mentioned above, by the use of nitroglycol or diglycerine tetranitrate; nitro-toluenes have also been introduced as constituents of some of these low-freezing dynamites.

CHAPTER IX

EXPLOSIVES MADE FROM COTTON

The Versatile Carbohydrates

CARBOHYDRATES could be called the Admirable Crichtons of organic chemistry. It is, indeed, a matter for wonder that substances with molecules composed essentially of strings of –CH(OH)– units can assume so many forms and functions. They are truly "built on a craftily complex plan, founded in deep simplicity". As sweet crystalline sugars and granular starches they are foodstuffs of the first importance for plants and animals alike, and in the form of fibrous celluloses they constitute the structural framework of the vegetable world. Celluloses of various types provide the raw material for the manufacture of fine and coarse textiles, ropes, string, and paper. Even the less amenable "incrusted celluloses" of woods are now used on an enormous scale in the production of artificial silk, films, aeroplane dope, imitation horse-hair and leather, and many other equally useful materials. Moreover, starches and even celluloses may be broken down into sugars and hence used as sources of power alcohol. The natural function of carbohydrates as storehouses of energy needs no further emphasis (p. 46). In brief, sugars and starches are indispensable to the inner man, and celluloses to the outer man. Without them there would be little food, no cotton or linen, and no newspapers: indeed, there would be no plants, no man, and no civilisation.

With so much to their credit, it is not surprising that these versatile substances are widely applied in making explosives. Cellulose, indeed, is one of the most important raw materials of the explosives industry, and starch is also used to some extent in the same way. Like glycerol—itself a carbohydrate frag-

ment (p. 90)—the carbohydrates are polyhydric alcohols, although of a more complex type. Accordingly, they are able to undergo esterification with the formation of alcohol nitrates, or nitric esters, fundamentally similar in constitution to the so-called nitro-glycerine (p. 91), and containing a repetition of the nitrate group, $-O\cdot NO_2$.

Many of the most familiar carbohydrates, such as glucose, cane sugar, potato starch, and cotton cellulose, possess molecules which are based upon a unit of six carbon atoms (C_6). Simple sugars of this kind, like glucose, have molecules containing one C_6–unit, the molecular formula being $C_6H_{12}O_6$. The molecules of such di-sugars as cane sugar, milk sugar, and malt sugar contain two C_6–units, and their molecular formula is $C_{12}H_{22}O_{11}$. The much more complex molecules of starches and celluloses are represented by the formula $(C_6H_{10}O_5)_n$, in which n may be several hundred for starches and still higher for cellulose.

Nitro-starch

Cane sugar may be nitrated, but the resulting "fulminating sugar"—a white powder soluble in water—is unsatisfactory as an explosive on account of its unstable nature and its tendency to absorb atmospheric moisture; moreover, sugar is an expensive raw material for such a purpose. Starch was nitrated so long ago as 1833 by Braconnot, who used nitric acid alone as the nitrating agent. In recent times a so-called **nitro-starch** of various degrees of nitration has been manufactured and used as an explosive, particularly in the United States. Nitro-starch is a white powder, insoluble in water; it absorbs moisture from the air much more readily than the nitro-celluloses. It is used in the United States as a blasting explosive, either alone or in admixture with sodium nitrate, wood meal, etc. It is also used as a constituent of some smokeless powders, and for filling hand and rifle grenades. It is said that nitro-starch may be manufactured more cheaply than nitro-glycerine in the United States, and that during the war of 1914–1918 its production in that country reached some 750 tons per month.

Cellulose Nitrates (Nitro-celluloses)

Cellulose enters into the explosives industry as a raw material, chiefly in the form of cotton waste, although wood cellulose is being used on an increasing scale. Cotton cellulose has the great advantage of uniformity of composition and texture. The ultimate source of cotton is cotton-wool, which consists of an intertangled mass of seed-hairs surrounding the seeds of the cotton plant: when spun into a yarn, these hairs form cotton. Each seed-hair consists of a hollow fibre, flat and twisted, and about an inch long. The short fibres left on the seed after the staple cotton has been removed are called "linters". Cotton cellulose is often called "normal" cellulose, in contrast to the "compound" celluloses of straw, jute, wood, etc., which yield varying amounts of modified celluloses when broken down by chemical treatment.

The normal, or standard, cellulose of cotton is represented by the complex molecular formula, $(C_6H_{10}O_5)_n$. For the present purpose, however, it is sufficient to consider a single unit, $C_6H_{10}O_5$, of the cellulose molecule, and to depict it as a trihydric alcohol unit, $C_6H_7O_2(OH)_3$. The molecular unit of cellulose then becomes closely analogous to the complete molecule of glycerol, $C_3H_5(OH)_3$. If such a unit were fully nitrated it would yield a trinitrate, corresponding to glyceryl trinitrate (nitro-glycerine); while a more gentle nitration might conceivably yield a dinitrate. For the sake of simplicity, the two celebrated explosives known as **guncotton** and **collodion cotton** may be represented approximately as cellulose trinitrate and cellulose dinitrate, respectively:

$C_3H_5(O\cdot NO_2)_3$	$C_6H_7O_2(O\cdot NO_2)_3$	$C_6H_7O_2\begin{pmatrix}O\cdot NO_2\\O\cdot NO_2\\OH\end{pmatrix}$
Glyceryl trinitrate ("Nitro-glycerine").	Cellulose trinitrate ("Guncotton").	Cellulose dinitrate ("Collodion cotton").

These representations of guncotton and collodion cotton are not exact. Both of these explosives are doubtless mixtures of

esters and not specific compounds. In practice, the nitrogen content of guncotton varies from about 13·0 to 13·5 per cent., whereas the above trinitrate formula demands 14·1 per cent.; also, collodion cotton contains on an average about 12 per cent. of nitrogen, and the dinitrate formula requires only 11·1 per cent. Thus, judged on the nitrogen content, guncotton is insufficiently nitrated for a trinitrate and collodion cotton is too fully nitrated for a dinitrate. The degree of nitration of the cellulose depends upon the conditions adopted in the particular experiment. In the manufacture of guncotton the nitration is made as complete as practicable in large-scale working.

These mixtures of cellulose nitrates are usually miscalled "nitro-cellulose". They have a wide range of uses besides their application in the explosives industry. These uses are determined largely by the nitrogen content of the preparation concerned. A low nitrate, containing sometimes even less nitrogen than a dinitrate, forms the basis of *celluloid*, or *xylonite*, one of the best-known synthetic plastics. Preparations with a somewhat higher nitrogen content are suitable for the production of "newskin" and "process collodion". In 1884, Count Hilaire de Chardonnet showed that a collodion of this type could be used in making a variety of *artificial silk*, the threads of cellulose nitrate being eventually denitrated to yield solid, structureless threads of cellulose; Chardonnet silk has now been displaced by other kinds of cellulose silks, such as viscose silk and acetate silk.

Collodion cotton used in various explosives may contain from about 11·5 to 12·7 per cent. of nitrogen. The uses to which a particular specimen of nitrated cellulose may be put depend upon its solubility in various solvents, as well as upon its nitrogen content, and these two factors cannot always be correlated: two specimens of cellulose nitrate having the same nitrogen content may differ widely in solubility. Collodion cotton is usually required to dissolve freely, or completely, in a mixture of 2 parts of ether with 1 part of alcohol, but guncotton is practically insoluble in this mixture. The following table gives a summary of some of these relationships; but it must not be interpreted too rigidly:

Percentage of Nitrogen	*Name*	*Solubility*	*Applications*
10·7—11·7	Collodion Cotton	Soluble in ether-alcohol; partly soluble in alcohol	Celluloid plastics; surgical and photographic collodion; Chardonnet silk, etc.
11·5—12·7	„	Soluble in ether-alcohol, acetone, nitro-glycerine, etc.; partly soluble in alcohol	Smokeless powders
13·0—13·5	Guncotton	Insoluble in ether-alcohol; soluble in acetone, ethyl acetate, amyl acetate, nitro-benzene, etc.	High explosive; smokeless powders

PROPERTIES AND APPLICATIONS OF CELLULOSE NITRATES (NITRO-CELLULOSES)

Guncotton

Guncotton is made chiefly from cotton waste, derived as a rule from spinning mills; cotton "linters" are also used. The waste is usually degreased by extraction with coal-tar benzene, or with petroleum benzine, and is then subjected to successive treatment with alkaline, bleaching, and acid liquors, after which it is washed with water and dried. Mechanical impurities are removed by hand-picking before and after it leaves a teasing machine, and the cotton is finally dried in hot air and allowed to cool off in closed iron bins.

The details of the nitration differ considerably in various factories, and for the present purpose it will suffice to describe one of the simplest processes in brief outline. This is a one-stage method known as the "direct dipping" process. The operation is carried out in iron nitrating pots known as "dippers";each pot is surrounded by cooling water and is closed by a lid carrying an exhaust pipe to take away acid vapours. The composition of the acid used in a particular nitration is determined by the period of nitration of the cotton: a quick nitration by this process may be carried out in 8 hours by using a nitrating mixture comparatively rich in nitric acid; but weaker acids may require twice or three

times as long in order to effect a similar degree of nitration. As an example, a suitable acid for a 12-hour immersion contains 15·75 per cent. of nitric acid and 75·0 per cent. of sulphuric acid, the remaining 9·25 per cent. being water.

The dipper is charged with 127 lb. of this acid, the temperature of which is brought to 15°. A charge of 4½ lb. of the prepared cotton is stirred gradually into the acid, the temperature being allowed to rise to about 25°. After 12 hours the resulting guncotton is freed as completely as possible from the acid by centrifugation, and is then transferred in small portions to a large washing tank through which a constant stream of running water is maintained. Each batch of guncotton is plunged very quickly into the water and pushed well below the surface with a wooden paddle; it is then kept in motion and washed until it is practically neutral in reaction, whereupon it is centrifuged and washed once more before being stabilised. The cotton increases markedly in weight during the process of nitration, a charge of 4½ lb. yielding more than 7 lb. of guncotton. The spent acid from the nitration is "fortified" or "revivified", and used again.

Formerly the purification of guncotton was not taken beyond this point. Many accidents occurred with the product, however, and researches due mainly to Sir Frederick Abel showed the necessity of a further treatment to remove lingering traces of acids or acid-forming substances. Such impurities are able to initiate a cumulative decomposition which may lead up to an explosion. Rigorous purification is essential for all explosives of the nitric ester type, containing the grouping $-O\cdot NO_2$. Guncotton is *stabilised* in a very simple way by subjecting it to a prolonged boiling with successive quantities of water, the treatment lasting sometimes for several days. In some factories additions of small amounts of certain chemicals are made to the water.

The stabilised guncotton is next reduced to a pulp of a suitable size, by beating it with water for several hours in a machine resembling the beaters used for paper pulp. The washed pulp is eventually separated from the bulk of the water by suction exerted on a wire gauze support, and is then squeezed into slabs by light hydraulic pressure, followed by a heavy pressure of 5 or 6 tons per square inch.

Moist slabs or cylinders of guncotton are very stable and safe to handle: indeed, they may be worked with tools in much the same way as blocks of wood. Such slabs, containing about 15 per cent. of water, may be fashioned into convenient shapes by sawing or turning, when they are required for use as primers; holes for the detonators are bored in the moist primers, which are then dried off and waterproofed by a rapid immersion in molten paraffin wax or a gelatinising solvent such as acetone or ethyl acetate.

Guncotton and other nitrated cottons retain the appearance and fibrous structure of the parent cellulose, but possess a rougher feel; all such materials are odourless, tasteless, and neutral in reaction. Stabilised guncotton, preferably in contact with water, may be kept indefinitely without deteriorating. Dry guncotton is soluble in acetone, ethyl acetate, amyl acetate or nitro-benzene; but it is insoluble in water, ether-alcohol mixtures, or nitro-glycerine. When loose and unconfined it burns suddenly and fiercely when ignited, but does not explode; moist guncotton slabs do not ignite.

Dry guncotton is fairly sensitive to shock, but when moist it is fairly insensitive. Partial detonation occurs when dry guncotton containing 13 per cent. or more of nitrogen is struck by steel on steel. Mercury fulminate detonates dry guncotton easily, but even a small amount of moisture necessitates a marked increase in the amount of fulminate required for this purpose. In practice. guncotton in bulk is always kept and used in a moist condition, This relatively safe and uninflammable form of the explosive may be detonated with ease by the use of a primer of dry guncotton in which a suitable detonator is embedded.

Guncotton is a powerful high explosive: the velocity of detonation of the dry material attains 7300 metres per second, and in a Trauzl test the observed expansion was 1·3 times as great as for picric acid in a parallel test. Since it suffers from a deficiency of oxygen it is less powerful than explosives like blasting gelatine, based upon nitro-glycerine. It is applied largely in the manufacture of smokeless powders; formerly it was also used extensively as a charge for torpedoes and submarine mines, but for these purposes it has been replaced by coal-tar explosives such as trinitrotoluene and amatol.

Collodion Cotton

Collodion cotton, sometimes known as "pyroxylin" or "soluble nitro-cellulose", is not a product of constant composition. Like guncotton, it consists of a mixture of nitrated celluloses which may vary within certain limits. In practice, a collodion cotton is often rated on its nitrogen content, although this is not an unfailing index to its properties; in particular, the solubility should be taken into account. For smokeless powders the nitrogen content is kept within a narrow range, from about 12·5 to 12·7 per cent., but for blasting explosives it may vary from about 11·5 to 12·3 per cent. The precise method of nitration that will provide a collodion cotton having the requisite properties has to be found by experiment; but in general the cotton is nitrated with a weaker and warmer acid, and for a shorter time, than in the production of guncotton. It may be steeped, for example, at 40° for 2 hours in a mixed acid composed of 23 per cent. of nitric acid and 66 per cent. of sulphuric acid, the remaining 11 per cent. being water. Washing and stabilisation are carried out as with guncotton, except that the water is kept at about 90°.

Collodion cotton resembles guncotton in appearance and feel. Good specimens, unlike guncotton, dissolve completely in a mixture of 2 parts of ether with 1 part of alcohol, forming viscid solutions; such specimens also dissolve completely in nitro-glycerine, as in the manufacture of blasting gelatine (p. 101). When loose and unconfined, collodion cotton burns fiercely and completely. It is not detonated by concussion, and it may be kept indefinitely in a moist condition.

Smokeless Powders

The chief uses of guncotton and collodion as explosive materials are in the manufacture of smokeless powders; collodion cotton also enters into the composition of certain very valuable blasting explosives, in admixture with nitro-glycerine (p. 102). Until about 1880 the only propellant used for military and sporting purposes was gunpowder; but with the advent of modern high-power explosives the invention of new and correspondingly powerful propellants was inevitable. The nitro-cellulose propellants are

superior to gunpowder not only in power, but also by reason of their smokeless nature, their definite rates of burning, and their resistance to damage by wetting.

The ideal propellant is an explosive which undergoes rapid, and, when required, progressive internal burning in such a way as to exert the maximum permissible pressure upon the projectile while it is in the gun. It must not, of course, be able to detonate under working conditions, or it would then shatter the gun. The strong and steadily exerted pressure should not be so great as to stress the gun unduly; moreover, the charge should be consumed by the time the projectile leaves the muzzle. These exacting demands cannot be met by gunpowder, although some degree of adjustment is possible by varying the size of grain and using perforated cake powders (p. 79). The nitro-cellulose powders have the advantage that they may be used in the form of uniform threads or tubes of any desired dimensions, thus permitting of a fine adjustment between the surface-area and the weight of the propellant: this leads in turn to a control of the rate of burning and the consequent pressure of the gases. For example, the charge of smokeless "powder" (cordite) in a rifle cartridge may be composed of about fifty small threads of the thickness of a darning needle: these burn much more quickly than the stout cords or rods used in a large gun, the long bore of which calls for a more leisurely and progressive rate of burning.

Guncotton and collodion cotton cannot be used as propellants in their fibrous form. When they are ignited in confinement the hot gases of the combustion are forced by the pressure into the pores of the unburnt material, and the rate of burning is progressively increased, so that an excessive and uneven pressure would be exerted upon the gun. The rate of burning may be reduced by compressing the nitrated cotton or by mixing it with certain inert materials or with cooling agents; but the most effective control is achieved by gelatinising the explosive, thereby rendering it non-porous.

The first service propellant of this type was **Poudre B,** adopted in France in 1886 (p. 85): this was made by gelatinising a mixture of guncotton and collodion cotton with ether-alcohol and working up the paste into small squares of a dry horn-like material;

modern military propellants are often used in a similar form. The British service propellants assume other forms, indicated by the descriptive name, "cordite". **Cordite Mark I,** first manufactured in 1890, was an incorporation of only 37 per cent. of guncotton with 58 of nitro-glycerine and 5 of mineral jelly (vaseline). The large proportion of nitro-glycerine gave a high temperature of explosion, which led in turn to serious erosion of the bore in large guns. In **Cordite M.D.,** introduced in 1901, the percentage of guncotton was raised to 65, at the expense of the nitro-glycerine (30). Owing to a shortage of acetone, used in the gelatinisation and incorporation, a new land service propellant, known as **Cordite R.D.B.,** was elaborated during the war of 1914-1918. This variety of cordite contains collodion cotton (52 per cent.) in place of guncotton, and the gelatinisation and incorporation can therefore be carried out with ether-alcohol in place of acetone; the ballistic properties are maintained by the increased proportion of nitro-glycerine (42 per cent.).

In the manufacture of cordites, the carefully dried guncotton or collodion cotton is first mixed by hand with the nitro-glycerine in a rubber-lined canvas bag, and the mixture is then rubbed through a coarse sieve. The resulting "cordite paste" is mechanically kneaded for several hours with acetone; mineral jelly is added, and the kneading is repeated. Enough acetone is used to dissolve the two main ingredients and incorporate them thoroughly with the vaseline. The viscid "cordite dough" is then transferred to presses and forced through suitable dies, so as to form threads, cords, or hollow tubes of the sizes required. The acetone remaining in the freshly-expressed cordite is recovered during the final drying process.

The smaller sizes of cordite are wound on reels forthwith, and the larger ones are cut into lengths. These large cords, superficially resembling rubber pressure-tubing, are capable of hurling projectiles of about a ton in weight through a distance of some thirty miles. The number of British service cordites expresses the diameter of the cords or rods in hundredths of an inch, ranging from size 3$\frac{3}{4}$ (0·0375 inch for rifles) to size 50 (0·5 inch, for large naval guns); size 20 is suitable for 4·7-inch and size 30 for 6-inch quick-firing guns.

Cordite varies from yellowish-brown to dark brown in colour. Some kinds resemble hard rubber, but others are brittle and easily fractured. The specific gravity is about 1·58. The material is non-porous, stable, and unaffected by water; it is also poisonous. When held in a flame, cordite takes fire very soon, and burns strongly with a vivid yellow flame, which is smokeless because the products consist entirely of invisible gases which "melt into the air". Cordite used as a propellant in heavy guns gives rise upon discharge (Plate IV) to large volumes of hot gases, consisting of carbon dioxide, carbon monoxide, steam, nitrogen, and small amounts of oxides of nitrogen. All of these are invisible except the steam, upon condensation, and the reddish-brown nitrogen peroxide. Sufficient free carbon is also produced, in a finely divided form, to give rise to a light smoke.

Cordite is very insensitive to shock, and withstands the passage of a rifle bullet without exploding: this, of course, is an important requisite in a service explosive. The fine threads of cordite used in small-arm cartridges can be fired with a strong percussion cap, but the stouter cords require an intermediate primer of gunpowder or guncotton. The explosive power of cordite is much greater than that of gunpowder, the maximum pressures attainable being about 120 tons and 40 tons per square inch, respectively.

Cordite thus fulfils the main requirements of a good propellant, its chief disadvantages being its erosive action on the bore of the gun and the brilliant flash of its discharge. In these respects, Cordite M.D. and R.D.B. are superior to the original Mark I. Some smokeless propellants contain "flash reducers", including metallic salts and wax, which act as *cooling agents* and reduce the temperature of the gases emerging from the gun-muzzle to a point below their ignition-point in air: if these hot explosion gases contain too much carbon monoxide they may also ignite when the breech is opened. Small quantities of *stabilisers*, including vaseline and diphenylamine, may also be added to increase the keeping properties of the propellants; furthermore, *moderants* or *deadeners*, such as camphor, castor oil, vaseline, or wax, are sometimes included to reduce the speed of the explosion.

All smokeless powders, whether military or sporting, are based

upon nitrated celluloses; the military powders often contain nitro-glycerine in addition. All small-arm powders except cordite are granular. The cellulose required for the manufacture of these powders is being increasingly obtained from wood, in place of the more expensive cotton.

Sporting powders produce a milder recoil and less noise than gunpowder. They do not often contain nitro-glycerine, but they have subsidiary ingredients such as metallic nitrates, dichromates, and nitro-hydrocarbons. They consist of flakes or grains of various sizes, usually grey, yellow, orange, or brown in colour, and are very resistant to detonation. *E.C. Powder No. 3*, for example, is composed of collodion cotton and guncotton, with mineral jelly, potassium and barium nitrates, and sometimes camphor and wood meal. This is a fibrous "bulk" powder for shot-guns, in which the propellant, only slightly gelatinised ("hardened") in loose grains, occupies the same space or bulk as black gunpowder used for the same purpose. "Condensed" powders occupy as little as one-third of this space, and are fully gelatinised.

The table below gives illustrative examples of the chief types of smokeless propellants, the first group differing from the second in containing no nitro-glycerine:

	E.C. Sporting Powder No. 3	*French Poudre B*	*Cordite Mark I*	*Cordite M.D.*	*Cordite R.D.B.*
Collodion Cotton	30·4	30	—	—	52
Guncotton ..	44	67	37	65	—
Nitro-glycerine ..	—	—	58	30	42
Mineral jelly ..	6	—	5	5	6
Diphenylamine ..	—	2	—	—	—
Camphor ..	4	—	—	—	—
Metallic nitrates	14	—	—	—	—
Moisture.. ..	1·6	1	—	—	—

COMPOSITIONS OF SOME SMOKELESS POWDERS

CHAPTER X

EXPLOSIVES MADE FROM COAL

The Treasures of Coal Tar

About the year 1690 the Rev. Dr. John Clayton, "Rector of Crofton at Wakefield in Yorkshire," sometime Dean of Kildare in Ireland, and an authority on the plants, natives, and other "Observables in Virginia", described a novel experiment with coal. In his own words, "I got some Coal which I distilled in a Retort in an open Fire. At first there came over only *Phlegm*, afterwards a black *Oil*, and then likewise a *Spirit* arose, which I could noways condense, but it forced my Lute, or broke my Glasses." He filled a good many bladders, "squeezed and void of Air", with this Spirit. "And when I had a Mind to divert Strangers or Friends," he continues, "I have frequently taken one of these Bladders, and pricking a Hole therein with a Pin, and compressing gently the Bladder near the Flame of a Candle till it once took Fire, it would then continue flaming till all the Spirit was compressed out of the Bladder."

Possibly—for this is the way of the world—the diverted Strangers and Friends thought their host an amiable crank; for their seventeenth-century minds were naturally unable to discern the germs of enormous industries lying dormant in this simple experiment. In later days the worthy Doctor's *Phlegm*, *Oil*, and *Spirit* became known severally as ammonia liquor, coal tar, and coal gas. The first of these coal distillates is an important source of fixed nitrogen for artificial fertilisers, the second is probably the most valuable raw material known to the organic chemist, and the third accounts at the present day for a capital investment in Great Britain alone of some £150,000,000.

In ordinary gasworks practice, when bituminous coal is heated in retorts, it yields on an average about 70 per cent. of residual coke, and the volatile products furnish about 17 per cent. of gas, 7 per cent. of ammonia liquor, and 6 per cent. of

coal tar. The thick black oil constituting the tar is a complex mixture of organic substances, of which only about a dozen are in common use as "primaries" (p. 87). The primaries are extracted from the tar by repeated distillation, supplemented by special treatment. The following table shows that the combined amounts of the five most important primaries form only about 7·4 per cent. of the tar, and thus about 0·4 per cent. of the weight of the original coal:

Substance	*Molecular formula*	*M.p.*	*B.p.*	*Approximate percentage yield from coal tar*
Benzene ..	C_6H_6	5·4°	80·4°	1·5
Toluene ..	C_7H_8	−98	110	
Phenol.. ..	C_6H_6O	42·5	183	0·5
Naphthalene ..	$C_{10}H_8$	80	218	5
Anthracene ..	$C_{14}H_{10}$	213	351	0·4

SOME IMPORTANT COAL-TAR PRIMARIES

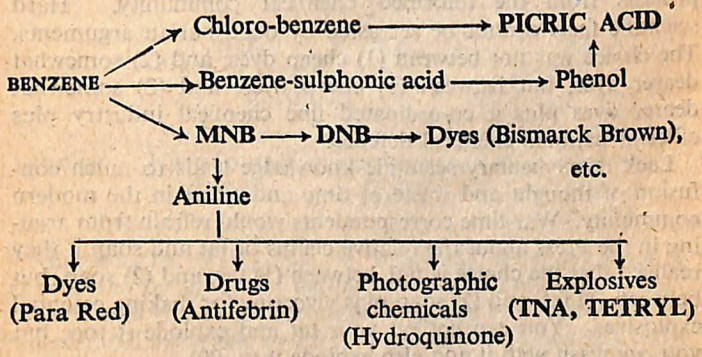
By treatment with various reagents, coal-tar primaries may be converted into "intermediates". Several hundred of these are in common use: from them, by means of further reactions, an enormous number of useful fine chemicals, known as "coal-tar derivatives", have been synthesised. Coal-tar dyes alone have been made by the thousand, and to these must be added large numbers of medicinal chemicals (drugs), antiseptics, photographic chemicals, explosives, and other fine chemicals having various applications. As *Punch* once remarked, in a moment of vision:

> "Oil and ointment, and wax and wine,
> And the lovely colours called aniline:
> You can make anything, from a salve to a star
> (If you only know how), from black coal tar."

Coal-tar explosives thus form one of many groups of fine chemicals which may be synthesised from coal-tar constituents. These groups of coal-tar derivatives are so closely interlocked

that a member of one group may often be regarded as a by-product in the preparation of a member of another group. Consequently, the manufacture of the members of any group, if conducted economically, must form part of a well-ordered scheme for the complete chemical utilisation of coal tar.

For example, when toluene is mildly nitrated it yields mono-nitrotoluene (MNT). Further nitration of this intermediate leads to the explosives known as dinitrotoluenes (DNT) and trinitrotoluene (TNT); but other operations carried out on the same intermediate (MNT) lead to dyes and also to novocaine, a very valuable synthetic drug. Again, the interdependence of various types of fine chemicals synthesised from coal-tar benzene is strikingly evident from the following diagram, in which explosives are shown in heavy type:



THE INTERDEPENDENCE OF COAL-TAR DERIVATIVES

Dyes, Explosives, Politics, and Argumentation

Among coal-tar derivatives, dyestuffs occupy the central position. Their manufacture is an industry of national importance. It is also an industry which calls for incessant research on the part of skilled organic chemists, whose training entails years of devoted work and study. The dyestuffs industry is a "key industry". It dominates the fabrication of textiles,

leather, paper, paints, inks and many other essential commodities. It is also closely bound up with the manufacture of service explosives.

During the war of 1914–1918 Great Britain was seriously handicapped in expanding the production of explosives because of the lack of a strong organic chemical industry, and a corresponding dearth of skilled organic chemists. After the war, the position was safeguarded, as a result of this unhappy experience, by a Dyestuffs Act which prevented Germany from resuming her pre-war practice of dominating the British fine chemical market by underselling. It says little for popular scientific acumen in Great Britain that the Government proposed to allow the Dyestuffs Act to lapse in January, 1937, and were only restrained from so doing at the last moment, after intensely vigorous protests from the informed chemical community. Hard scientific facts cannot be set aside by doctrinarian arguments. The choice was not between (1) cheap dyes, and (2) somewhat dearer dyes, but between (1) cheap dyes, and (2) somewhat dearer dyes plus a co-ordinated fine chemical industry plus efficient national chemical defence.

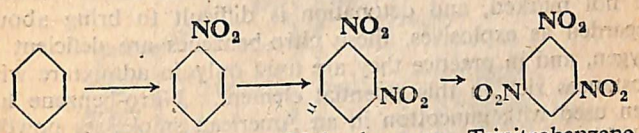
Lack of elementary scientific knowledge leads to much confusion of thought and waste of time and effort in the modern community. War-time correspondents would refrain from arguing in the Press about the relative claims of fat and soap if they realised that the choice is not between (1) fat, and (2) soap, but between (1) fat, and (2) soap plus glycerine for making essential explosives. You can *not* eat your fat and explode it too; but you *can* wash with it and also explode it (p. 90).

Nitro-benzenes

Benzene, C_6H_6, sometimes called *benzole*, and not to be confused with "petroleum benzine", is the most important coal-tar primary. It is a colourless, inflammable liquid, b.p. 80·4°, immiscible with water; like toluene and naphthalene, it is a hydrocarbon. Besides their occurrence in coal tar, both benzene and toluene are found in Borneo petroleum, which has therefore been used as a supplementary source of some of the so-called

"coal-tar explosives". Benzene is less important than toluene as a source of explosives. Upon nitration it readily yields mono-nitro-benzene (MNB, usually known as nitro-benzene) and di-nitro-benzene (DNB); but the much more powerful tri-nitro-benzene (TNB) is obtained only with great difficulty.

The nitro-benzenes, like the nitro-toluenes, picric acid, and other coal-tar explosives obtained by nitration, are true nitro-compounds containing the grouping C–NO_2 (p. 52). They are less powerful but more stable explosives than the nitrates, or nitric esters, such as "nitro-glycerine" and the "nitro-celluloses". The relative positions of the nitro-groups in the benzene ring (p. 30) is as follows for the particular nitro-benzenes in use as explosives, the specific dinitrobenzene here concerned being known as *meta*-dinitrobenzene, or 1, 3-dinitrobenzene:



Benzene — Nitro-benzene (MNB) — Dinitrobenzene (DNB) — Trinitrobenzene (TNB)

Nitro-benzene, $C_6H_5{\cdot}NO_2$, is very easy to prepare on a small scale, by gradually adding, with gentle shaking, a cold mixture of 4 c.c. of concentrated sulphuric acid and 3 c.c. of concentrated nitric acid to 2 c.c. of benzene contained in a small flask. The temperature is allowed to rise to 50°, and after a few minutes the yellowish liquid is poured into an excess of cold water. Nitro-benzene separates as a heavy, pale yellow oil, with an odour of bitter almonds:

$$C_6H_6 + HO{\cdot}NO_2 = C_6H_5{\cdot}NO_2 + H_2O.$$

It is used as a cheap scent for soap under the name of "oil of mirbane". The vapour is poisonous, and when inhaled continuously produces cyanosis, or lividness of the skin, caused by imperfect oxidation of the blood. The effect is produced in

general by the vapours of aromatic (p. 29) nitro-compounds. Nitro-benzene is an intermediate of the first importance, being used, for example, in the manufacture of aniline (p. 128).

Dinitro-benzene, $C_6H_4(NO_2)_2$, may be prepared for purposes of demonstration by adding from 0·5 to 1 c.c. of nitro-benzene, drop by drop, to a cold mixture of 3 c.c. of concentrated sulphuric acid and 2 c.c. of fuming nitric acid in a wide test-tube, with shaking. The liquid becomes very hot, and when it is poured, after about a minute, into an excess of cold water a crystalline deposit of dinitro-benzene separates out. The crude product melts at about 86°, but pure *meta*-dinitro-benzene melts at 90°. It has a poisonous action closely similar to that of trinitrotoluene, described below. Although very stable to shock (p. 65), it is liable to explode when heated suddenly.

The explosive properties of nitro-benzene and dinitro-benzene are not marked, and detonation is difficult to bring about. Regarded as explosives, these nitro-benzenes are deficient in oxygen, and in practice they are used only in admixture with substances rich in this essential element. Nitro-benzene has been used with guncotton in an American smokeless powder called *Indurite*. With potassium chlorate, it enters into the composition of some kinds of *Cheddite* (p. 81); moreover, a mixture of potassium chlorate and nitro-benzene (21 per cent.) is known in the United States by the expressive name of *Rack-a-Rock*. This blasting explosive was used, in 1885, in removing the Hell Gate reefs from the channel of East River, New York, and also in the construction of the early Chinese railways. It may be included among the so-called **Sprengel explosives**: these are mixed explosives made *in situ*, as needed, from constituents which by themselves are quite safe and easy to handle and transport. In this instance, weighed amounts of potassium chlorate in cotton containers are steeped in nitro-benzene until the required weight of the liquid has been absorbed. **Trinitro-benzene,** a crystalline solid, m.p. 121–122°, is a more powerful explosive than dinitro-benzene, or even trinitrotoluene; but it is difficult to make and little used as an explosive. Its velocity of detonation in pellet form is about 6700 metres per second, compared with 6100 for dinitro-benzene. In a Trauzl

test the expansion was intermediate between the values observed for trinitrotoluene and picric acid.

Nitrating-pots

In technical practice the nitration of benzene, toluene, phenol, etc., is carried out in a cast-iron nitrating-pot with a domed

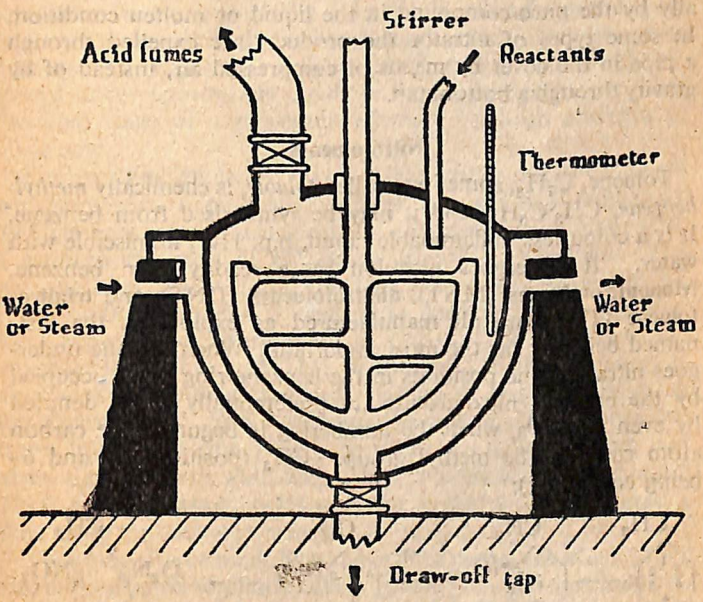


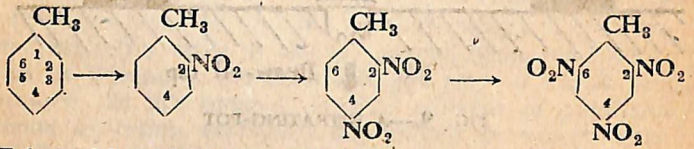
FIG. 9.—A NITRATING-POT

cover, of which a simple type is shown diagrammatically in Fig. 9. The amount of nitric acid in the mixed acid is cut to the working minimum for the specific operation, and the residual "spent acid", consisting chiefly of sulphuric acid, is usually concentrated or suitably fortified for further use. Good admix-

ture is ensured by the use either of a mechanical stirrer or of compressed air, as in the nitrator-separator (Fig. 7). Either an external jacket (Fig. 9), or internal coils (Fig. 7), may be used to control the temperature, through the circulation of cold water, hot water, or steam. There is also an exhaust pipe conducting acid fumes to a recovery tower. At the end of the nitration the pot is used as a separating-funnel, the hot, spent acid being removed through the draw-off tap, followed eventually by the nitro-compound in the liquid or molten condition. In some types of nitrator the products are expelled through a pipe in the cover by means of compressed air, instead of by gravity through a bottom tap.

Nitrotoluenes

Toluene, C_7H_8, sometimes called *toluole*, is chemically *methylbenzene*, $CH_3{\cdot}C_6H_5$, and it may be synthesised from benzene. It is a colourless, inflammable liquid, b.p. 110°, immiscible with water. It undergoes nitration more readily than benzene. **Mononitrotoluenes** (MNT), **dinitrotoluenes** (DNT), and **trinitrotoluene** (TNT) are all manufactured as explosives, the last-named being by far the most important. When toluene undergoes nitration, the positions in the benzene ring to be occupied by the entering nitro-groups are preferentially those denoted by even numbers, when the numbering is begun at the carbon atom carrying the methyl group, $-CH_3$ (positions 2- and 6- being equivalent):



Toluene — Mononitrotoluenes (MNT) [2- or 4-] — Dinitrotoluenes (DNT) [2,4- or 2,6-] — Trinitrotoluene (TNT) [2,4,6-]

Technical mononitrotoluene is an oily liquid consisting essentially of a mixture of 2-nitrotoluene and 4-nitrotoluene; it

forms a constituent of certain blasting explosives and smokeless powders. 2,4–Dinitrotoluene, m.p. 70°, has similar uses.

These lower nitro-derivatives of toluene are formed in the earlier stages of the nitration process leading to trinitrotoluene. The trinitration is carried out in stages. For example, to a charge of about a ton of toluene in the nitrating-pot is added gradually about 3·3 tons of a nitrating acid containing about 62 per cent. of sulphuric acid and 21 per cent. of nitric acid, the remainder being water; the mixture is stirred continuously and kept at 35° throughout the addition, which takes from 3 to 6 hours. The waste acid is then run off, and the crude MNT is stirred under appropriate conditions with the spent acid from the final stage of a preceding nitration, with an addition of nitric acid.

The resulting crude DNT is then run into a nitrator charged with somewhat more than 5 tons of a mixed acid containing 79·5 per cent. of sulphuric acid and 17·8 per cent. of nitric acid, a temperature limit of 66° being observed meanwhile. The temperature is afterwards allowed to rise at a carefully controlled rate to 100°, at which it is kept until a specimen of the resulting TNT shows a wet setting-point (w.s.p.) of 72·5°. Owing to the appreciable solubility of TNT in the spent acid, the charge is diluted at 90° with a standard quantity of water at the same temperature; it is then transferred to a separator, whence the upper layer of molten TNT is removed to a tank in which it is given a preliminary wash with a little boiling water. The crude TNT, weighing about twice as much as the original toluene, is then ready for the final washing.

TNT may also be made by a continuous process in which MNT and concentrated sulphuric acid are passed in opposite directions through a series of nitro-separator pairs, the necessary nitric acid being injected at appropriate points in the chain: TNT thereby flows continuously from one end of the plant and spent acid from the other end. A plant of this type can deliver so much as 500 tons of crude TNT per week, at a very economical cost, from 250 tons of toluene and 500 tons of nitric acid.

Sometimes the same counter-current principle is adopted in the ensuing washing of the crude TNT with hot water, an operation

which has to be carried out very thoroughly. The molten TNT is drawn off from the final wash water and dried by passing it in a thin film along a wide steam-heated channel; it is then flaked from a bronze cooling-drum, rotating under a knife-edge, and is finally stored in bags.

For some purposes the TNT may be used without further purification. Besides 2,4,6–trinitrotoluene, or α–TNT, it contains small amounts of other trinitrotoluenes and traces of dinitrotoluenes (all with a nitro-group in a position with an odd number). These impurities give rise to an objectionable oily exudation from block TNT; they are best removed by treatment with sodium sulphite solution, which converts them into soluble sulphonates. After a final washing and flaking, TNT purified in this way has a dry setting-point (d.s.p.) of 80·5–80·6°.

α–TNT is a very stable, pale-yellow solid, melting at 81°. When heated in the open to about 250° it takes fire and burns with a hot and very sooty flame, but does not explode when present only in small quantity. It is not exploded by the impact of a rifle bullet, and it is so insensitive to shock that it may be used in armour-piercing projectiles in which a delayed explosion is essential (p. 147).

In the form of powder or loose crystals it undergoes detonation with mercury fulminate of a No. 3 detonator (p. 145); but in block form it requires a gaine of its own powder, or of tetryl, etc. The velocity of detonation reaches 6700 metres per second in the latter form. A Trauzl test gave an expansion of 310 c.c. (picric acid, 350 c.c.). Its stability, power, and certain response to detonation under standard conditions render TNT an explosive of the first importance, and since the war of 1914–1918 it has been used extensively as a service high explosive. The wide adoption of this explosive is indicated by its many synonyms, which include such names as *Trilit*, *Trinol*, *Tritolo*, *Triton*, *Trolite*, *Trotyl*, and *Füllpulver–02* (*Fp–02*). Its main use is as a bursting charge in shells, bombs and mines. If used alone it may be melted with live steam and poured into the receptacle.

Owing to its very marked deficiency in oxygen, TNT is more often used in admixture with substances rich in oxygen, notably with ammonium nitrate. *Amatol*, introduced in 1915 as a bursting

charge, may contain so much as 80 per cent. of ammonium nitrate to 20 per cent. of TNT; besides its high efficiency, this explosive has the advantage of relative cheapness, since ammonium nitrate costs much less than TNT, which ranks as a fine chemical. Certain varieties of *ammonal* (p. 81) also contain TNT, and it is sometimes used in detonators.

Like other nitro-hydrocarbons used as explosives, TNT gives rise to undesirable physiological effects. Workers exposed to its vapour or dust are liable to suffer from cyanosis, dermatitis, and general poisoning, unless proper precautions are taken. Dust-control is of great importance in TNT factories, and the skin should be protected by the use of masks, gloves, and overalls.

Nitro-naphthalenes, made by nitrating naphthalene ("moth balls"), $C_{10}H_8$, are solid crystalline substances used to some extent as ingredients of explosives, as, for example, in *cheddite* and *ammonite* (p. 81).

Picric Acid (Lyddite)

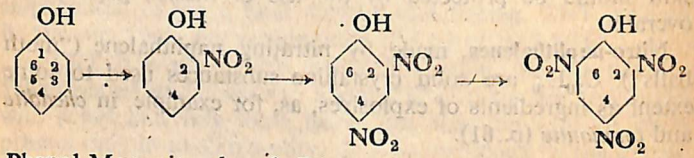
Phenol, also known as *carbolic acid*, is the only coal-tar primary of the first importance (p. 116) which contains oxygen. Chemically, it is *hydroxy-benzene* $HO{\cdot}C_6H_5$. It is the starting-point in the synthesis of a very large number of dyes, drugs, and other fine chemicals (including phenolphthalein, aspirin, and phenacetin); it is used also in the manufacture of bakelite, a common synthetic plastic. The most important explosive compound derived from phenol is picric acid, or trinitrophenol, which is known as a high explosive under the names of *Lyddite*, *Melinite*, *Shimose*, *Pertite*, *Picrinit*, etc. The close interdependence of coal-tar explosives, dyes, and medicinal chemicals has already been emphasised: picric acid itself has a triple use as an explosive, a dye, and a remedy for burns.

Picric acid appears to have been discovered in 1771 by Woulfe, who obtained it by heating indigo with nitric acid; Hausmann prepared it in a similar way in 1788; and in 1799 Welter introduced it as the first artificial dye—it dyes wool and silk bright yellow from a warm aqueous bath. On account of its bitter taste it became known as "Welter's bitter"; the name "picric"

acid, derived from the Greek, records the same characteristic of the substance. In 1841 Laurent showed that it could be obtained by nitrating phenol, and thus picric acid was seventy years old before it became a coal-tar derivative.

During the war of 1914–1918 the supply of "straight" coal-tar phenol for the manufacture of lyddite was supplemented by "synthetic" phenol prepared from benzene; moreover, benzene was converted into picric acid by another process which did not include phenol as an intermediate stage (p. 117).

The nitration of phenol is fundamentally similar to that of toluene, the even positions being preferentially occupied by the nitro-groups:



Phenol — Mononitrophenols [2– or 4–] — Dinitrophenols [2,4– or 2,6–] — Picric acid [2,4,6–Trinitrophenol]

The lower nitrophenols enter only to a subordinate extent into the manufacture of certain composite explosives, but they are important intermediates.

In the ordinary method of manufacturing picric acid, molten phenol is poured into about 4 times its weight of concentrated sulphuric acid contained in a steam-jacketed iron pot, fitted with a stirrer, the temperature being kept at about 70° for 4 hours. The resulting solution of sulphonated phenol is then nitrated in jacketed nitrating-pots of enamelled iron, the original temperature of 20° being allowed to rise to about 80° during the addition of the nitric acid. After 2 hours' further stirring, the spent acid is removed, and the crystalline picric acid is collected by filtering, washed thoroughly with cold water, filtered with suction, and dried by centrifugation and stoving under steam-heat. The spent acid, as usual, is concentrated and used again.

In the last stage of the manufacture, contact with metals

must be avoided, as metallic picrates are sensitive to shock. For the same reason, shells used for picric acid are varnished on the inside, and the presence of basic materials, such as lime-mortar, must be avoided in buildings used for the storage of lyddite. Lead picrate is particularly sensitive to detonation by shock or heat. Picric acid does not cause dermatitis; but the dust and vapour act as irritants, besides imparting a yellow stain to the skin, hair, or clothing.

Picric acid forms yellow leaflets or needles, melting at 122°. It dissolves sparingly in water, forming a yellow solution. When heated in small quantities in the open, it takes fire at about 260° and burns fiercely without exploding; if traces of basic materials are present it may explode, and when heated with a little litharge it detonates violently (p. 62). It is also liable to explode on coming into contact with a red-hot surface.

It was not until a hundred years after the discovery of picric acid that Sprengel, in 1871, showed its explosive power upon detonation. In 1885 Turpin introduced it as a bursting charge in hollow projectiles, and soon afterwards it was generally adopted for this purpose. Since about 1915, however, it has been largely replaced by safer high explosives, such as amatol.

Pure picric acid is fairly insensitive to shock (p. 64). In dry powder form it can be detonated by a 1·5-gram charge of mercury fulminate, but in block form it is much more resistant to detonation; wet picric acid can be detonated only by using a suitable gaine, such as a little of the dry powder form. The oxygen-deficiency of picric acid is less than that of trinitrotoluene, and it is accordingly a more powerful explosive, although less powerful than blasting gelatine, as the following summary shows (Avogadro, 1931):

	TNT	*Picric acid*	*Blasting gelatine*
Temperature of explosion	2800°	3320°	4300°
Velocity of detonation (metres per second)..	6700	7100	7800
Trauzl test	310 c.c.	350 c.c.	620 c.c.

THE EXPLOSIVE POWER OF PICRIC ACID

In spite of its lower power, TNT is preferred to picric acid as an explosive because of its lack of acidic properties and consequent greater safety; moreover, unlike picric acid, it can be melted by the use of live steam, for pouring into shells, casting, and admixture.

Explosives from Aniline

Aniline traces its ancestry through nitro-benzene back to the coal-tar primary, benzene (p. 118). It is a substance used in manifold ways in the manufacture of dyestuffs and medicinal chemicals; it gives rise also to several explosives, of which the most important is *Tetryl*, or *Tetralite*. Since the scientific name of tetryl is *N*–nitro–*N*–methyl–2,4,6–trinitraniline, it is not surprising that this service explosive is known as *Composition Exploding*, or *CE* for short. It is a pale-yellow powder, m.p. 131°, made by the action of nitrating acid on a solution of dimethyl-aniline in concentrated sulphuric acid. When pure it is very stable, but it undergoes detonation fairly readily, so that it is used a great deal as a primer, or booster, in detonators. In a Trauzl test it gave an expansion of 375 c.c., compared with 320 c.c. for picric acid.

2,3,4,6-*Tetranitraniline*, or *TNA*, is a yellow solid, m.p. 220°, made by nitrating aniline in presence of concentrated sulphuric acid. This explosive displays a strong brisance, and the Trauzl expansion is no less than 415 c.c. (tetryl, 375 c.c.). Its density is 1·867, which is the highest value for any purely organic high explosive. It is slowly decomposed by boiling water.

Hexyl, or hexanitrodiphenylamine, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_2(NO_2)_3$, is another descendant of aniline, used as a constituent of high explosives for bombs, mines, etc. It is a yellow and very poisonous powder. In admixture with about half its weight of TNT it constitutes the high explosive *Novit*.

Cyclonite, also known as *Hexogen* or *T4*, was discovered in 1899. It may be regarded as a descendant of coal, although not of coal tar. It is prepared by the action of very concentrated nitric acid on a white crystalline substance, $(CH_2)_6N_4$, known variously

as hexamine, urotropine, or hexamethylenetetramine (HMT). The descent of cyclonite from coal may be traced briefly as follows: coal ⟶ coke ⟶ water-gas ⟶ methyl alcohol (methanol) ⟶ formaldehyde ⟶ hexamine ⟶ cyclonite. The molecule of cyclonite, $C_3H_6O_6N_6$, contains a six-membered ring-system in which the groups $-CH_2-$ and $-N(NO_2)-$ are arranged alternately. The substance is a crystalline solid, m.p. 203.5°. It is an explosive of unusual power and brisance, and has been suggested for use in bursting charges and also as a blasting and initiatory explosive. The detonation equation is given as follows:

$$C_3H_6O_6N_6 = 2CO + CO_2 + 2H_2O + H_2 + 3N_2.$$

CHAPTER XI

EXPLOSIVES THAT EXCITE OTHERS

The Two Kinds of Molecular Fifth Columnists

IN the fruitful field of international unrest there are two kinds of fifth columnists. One kind works within the agitated country, and the other exerts its influence from without, often by the use of wireless waves. A strikingly similar position holds in the field of explosive unrest. Here, the fifth columnists lurking and working within the molecular community of atoms are usually nitro-groups (p. 52): their sphere of operations is defined if we call them intra-molecular fifth columnists. But fifth columnists of another kind operate *outside* the frontiers of the molecule: these may be called *extra*-molecular fifth columnists. When the intra-molecular agitators have promoted the uneasiness of their fellow atoms to a sufficient pitch, their outside brethren come into action with a wireless wave of a particular length, to which the quivering molecule responds by collapsing in a sudden and violent disintegration, commonly known as an explosion.

These outside agents are usually called **initiatory explosives**, and their particular kind of wireless wave is known as a detonation wave. The commonest initiatory explosives, or exciting detonants (p. 58), are mercury fulminate and lead azide. These two substances are of a new molecular type, in that the central position in the molecule of each of them is occupied by a metallic atom. Besides these somewhat freakish compounds, other initiatory explosives of a more formal organic nature are known. The most important members of this literally exciting group now call for consideration.

Mercury fulminate

On March 13th, 1800, Edward Charles Howard, F.R.S., reported to the Royal Society upon "a new fulminating mercury"

which he had discovered. Like his more famous contemporary, Henry Cavendish, F.R.S., he was a member of a noble English family with a strong interest in science: his brother was the twelfth Duke of Norfolk. The spectacular properties of mercury fulminate (Latin, *fulmen* lightning) soon became evident, for Howard was seriously injured in the course of his researches on this choleric compound; however, like his far-off kinsman of Tennyson's ballad, he could swear he was "no coward", and his work in this strange and dangerous field soon led to a great development in the use of firearms (p. 140).

Mercury fulminate is the mercury salt of a curious organic acid containing only four atoms in its molecule—one each of carbon, hydrogen, oxygen, and nitrogen. The nitrogen atom is linked to oxygen on one side and to carbon on the other, as shown in the formula C:N.OH, and the instability of metallic fulminates is due partly to the carbon atom being forced to play the uncongenial and uneasy rôle of a bivalent atom. Silver fulminate, which is used in tiny charges in toy fireworks and crackers, was known in the seventeenth century, but it is too sensitive for general use. "When it is once obtained, it can no more be touched," wrote Nicholson, referring to its "terrible property," in 1795. Mercury fulminate is much safer to handle than silver fulminate, when the proper precautions are taken, and it is used extensively in cap compositions, for the ignition of propellants, and also in detonators to start off high explosives. It is largely on this account that mercury is in great demand in time of war. Mercury fulminate is usually represented by the formula $Hg(ONC)_2$, and this may be expanded as follows:

C:N.O.Hg.O.N:C
Mercury fulminate.

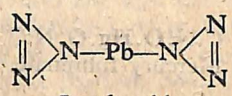
Mercury fulminate is made by dissolving mercury in concentrated nitric acid and pouring the warm solution into alcohol, under carefully defined conditions, in a roomy and suitable apparatus. After an initial period of quiescence a stormy reaction of a complex nature sets in, and eventually mercury fulminate begins to separate in small grey needles. At the end of the reaction the cooled mother-liquor is decanted and

the fulminate is collected on a filter and well washed with cold water. Large crystals are removed by passing the product through a fine screen, and the screened product is washed again until it is quite free from acid. The brownish-grey crystals obtained in this way are usually stored in linen bags under water. The density of the crystals is about 4·3.

The dry crystals are very sensitive to shock or friction; they detonate violently, for example, when struck by a hammer on an anvil. In the falling weight test, a fall of 4 cm. is sufficient to cause explosion with a 2-kg. weight. Large crystals, or clusters of crystals, are more sensitive than small ones, and are therefore rejected from commercial preparations. Detonation may also be brought about by heat, an electric spark, or contact with certain chemicals, including concentrated sulphuric acid. The explosion is very sharp, and its effect extremely local. Although mercury fulminate is used so widely it has certain disadvantages as an initiatory explosive, notably its liability to be affected unfavourably by moisture or by high compression. Small amounts may be destroyed by treatment with ammonium sulphide solution, larger quantities by burning in a train with paraffin oil.

Lead azide

Mercury fulminate later found a brother-in-arms in another still more curious explosive known as lead azide. This contains no carbon, no hydrogen, and no oxygen, its molecule consisting of a lead atom linked to six nitrogen atoms in two clusters of three:



Lead azide

This molecule cannot be made, as might be supposed, by the direct interaction of metallic lead and gaseous nitrogen: on the contrary, the structure has to be built up stage by stage. The ancestry of lead azide may be traced back to the four very familiar and distinctive substances, metallic sodium, ammonia gas,

laughing gas (nitrous oxide), and sugar of lead (lead acetate). When ammonia gas is passed over heated sodium it yields sodamide, $NaNH_2$. This, in turn, when heated in a stream of nitrous oxide, gives rise to sodium azide, NaN_3. A double decomposition with lead acetate in a well stirred aqueous solution finally leads to the deposition of fine white crystals of lead azide: sodium azide + lead acetate = sodium acetate (soluble) + lead azide (insoluble).

As with mercury fulminate, large crystals of lead azide must be avoided, as they are liable to explode when broken. Lead azide is less sensitive to shock or friction than mercury fulminate, and it maintains its sensitivity when moist, which is a great advantage. It is claimed that a charge of only 0·08 g. of lead azide is sufficient to detonate trinitro toluene, whereas the minimum amount of mercury fulminate required for the same purpose is about 0·35 g.

Lead azide thus possesses marked advantages over mercury fulminate. However, no explosive is perfect: lead azide is less readily ignited than mercury fulminate, and when used in a copper percussion cap it is liable to give rise to small amounts of copper azide, which is dangerous owing to its high sensitivity. The azides of silver, cobalt and nickel are also too sensitive to heat and friction to be of practical use, while others are unsuitable because of their solubility in water.

Tweedledum and Tweedledee

Mercury fulminate and lead azide are related in much the same way as Tweedledum and Tweedledee. Both of them are widely used as ingredients in cap compositions and as detonating agents for high explosives. Originally mercury fulminate held the field, but it has been displaced to some extent by lead azide. Each of them has its peculiar advantages and disadvantages, as indicated above.

Both compounds differ from all the commonly used explosives hitherto described in being endothermic. The formation of a gram-molecule (284 g.) of mercury fulminate from its elements corresponds to a heat absorption of 64,500 calories, and a gram-

molecule of lead azide (295 g.) has an even greater store of 100,600 calories of hoarded energy. Lead azide belongs to the group of non-oxidative explosives, like acetylene (p. 38), and its equation of detonation may be written as follows:

$$Pb(N_3)_2 = Pb + 3N_2 + 100{,}600 \text{ cals.}$$

It has been found by direct measurement that a gram of lead azide upon explosion liberates 360 calories of heat, and that the temperature of explosion is about 3500°.

Mercury fulminate is partly an oxidative but mainly a non-oxidative explosive, its equation of detonation being:

$$Hg(ONC)_2 = Hg + N_2 + 2CO + 116{,}900 \text{ cals.}$$

The contribution made by the oxidative part of the reaction is 52,400 calories. The temperature of explosion is again very high, as may be inferred from the above thermochemical equation.

Reference has been made earlier (p. 58) to the behaviour of these two explosives upon ignition. Their sharply localised action is bound up with the character of their explosion gases. These consist wholly or largely of vaporised metal and nitrogen gas, the elementary molecules of which quickly assume their final form. Steam and carbon dioxide, on the other hand, possess less molecular rigidity and may thus pass through intermediate delaying stages which impart a certain elasticity to explosion processes in which they are concerned.

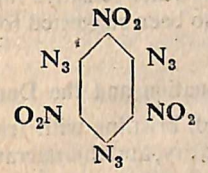
Organic Explosion-mongers

Of various organic substances which have been proposed for use as initiators, one of the most conventional in structure is **styphnic acid**, $C_6H(NO_2)_3(OH)_2$, the lead salt of which is sometimes used in cap compositions. Styphnic acid or trinitroresorcinol, is a near relative of picric acid, an extra hydroxy-group being present in position 3 (p. 126). It is obtained by nitrating resorcinol (which is readily made from benzene), and forms yellow prisms, m.p. 178°. The lead salt is an orange-yellow crystalline solid, less

sensitive to impact than mercury fulminate or lead azide; it detonates violently at 260°.

Hexamethylenetriperoxidediamine, otherwise HMTD, is a white powder obtained by the action of hydrogen peroxide on hexamethylenetetramine (HMT, p. 128) in presence of citric acid. It is considerably more sensitive to impact than mercury fulminate. Its molecule offers the unusual spectacle of two nitrogen atoms joined by three similar strings of atoms: $N(CH_2 \cdot O \cdot O \cdot CH_2)_3N$.

Trinitrotriazidobenzene, $C_6O_6N_{12}$, passes from the spectacular to the freakish, its molecular structure being represented as follows:



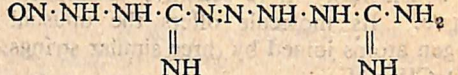
Trinitrotriazidobenzene

The original six hydrogen atoms of the benzene ring have been replaced by nitro-groups and azido-groups, the latter being identical in structure with those of lead azide. The preparation sets out from aniline and proceeds via trichloro-aniline, trichlorobenzene, and trichlorotrinitrobenzene, which yields greenish-yellow crystals of the above compound when treated with alcoholic sodium azide. TNTAB, as it will presumably be called if it becomes sufficiently popular, is less sensitive than mercury fulminate. It resembles mercury fulminate in being partly an oxidative and partly a non-oxidative explosive, the hoarded energy of the three disrupted azido-groups being added to the heat of formation of the six molecules of carbon monoxide when the molecule undergoes destructive collapse:

$$C_6O_6N_{12} = 6CO + 6N_2.$$

Tetracene, also known as *tetrazene* or guanylnitrosoaminoguanyltetracene, is the most bizarre of this selection of the

"slithy toves" and "mimsy borogoves" of organic chemistry. It consists mainly of nitrogen, and its formula, $C_2H_8ON_{10}$, has the appearance of an organic chemical scrap heap, or bargain basement. The 21 atoms are disposed in this strange molecular family as shown below:



Tetracene

Tetracene is a yellow solid, somewhat more sensitive to percussion than mercury fulminate. Other sensitive high explosives, cyclonite for example, have also been suggested for use as initiators.

Detonation and the Damsel

A chapter of this kind, bristling with frisky compounds, may well end with a striking story, and this narrative is literally striking as well as being true.

Once upon a time, now many years ago, a worthy Professor of Chemistry was lecturing in an Australian university. His subject was mercury fulminate. It was a very hot and humid day in November; his lecture theatre was filled to capacity with a hundred and seventy frisky young Australians, and it had a galvanised iron roof upon which the sun shone from a cloudless sky. Through the windows came incessantly the vibratory shrilling of the cicadas, or "bush canaries", mingled with the odour of sunbeaten eucalyptus leaves.

Now in this audience the young ladies sat in the front seats, immediately facing the lecture bench, and upon this torrid day of early summer one of them in particular was feeling the heat and humidity. As the lecturer wended remorselessly onwards, after the manner of professors immersed in their subjects, the distressed damsel became increasingly aware of the oppressiveness of her environment. At last the Professor warmed to his climax—a long-anticipated experiment on the detonation of mercury fulminate.

"You will observe on the anvil," came the familiar and

untiring voice, "a specimen—a very small specimen—of this powerful explosive, mercury fulminate. I am now about to strike it with a hammer. I invite you all, ladies and gentlemen, to pay attention to the result, and to recall in so doing what I have told you about the activating effects of the detonation wave—which I regret I cannot demonstrate to you as well."

The hammer fell.

The Professor had been too modest in his closing words. The experiment succeeded beyond his expectations. For when the hammer fell, the fulminate detonated with a loud report, and simultaneously the aforesaid damsel, seated in close proximity to the centre of disturbance, swooned away, after the manner of agitated young ladies.

The Professor, jerked out of his wonted self-possession by this unwonted response to the detonation wave, unwisely called for volunteers to carry the fair victim of detonative aggression out of the crowded room.

The Australians are a gallant race. The response was all that could have been expected, even in this Queen City of the South; for the eager class volunteered *en masse*, headed by the brawny captain of the University Rugby Football XV, the gigantic and lion-hearted Jumbo Woods. Having successfully removed the fainting lady, the class "called it a day".

On the following morning the Professor met his class again. There was a full attendance, including the heroine of the detonation wave. To the surprise of the class, the anvil still reposed on the lecture bench, and the Professor opened his lecture by taking up the hammer.

"It occurs to me, ladies and gentlemen," he began, "that owing to an unfortunate incident at the close of our last lecture you may not have grasped the full significance of the detonation of mercury fulminate. I am therefore about to repeat the experiment. But before I do so, I now afford anyone suffering from weak nerves an opportunity of leaving the room."

The Professor paused, with the uplifted hammer in his hand, and gazed pointedly at the innocent cause of yesterday's interrupted lecture. She, however, was feeling quite at her ease: a "southerly buster" had come up the coast in the afternoon, and

the room was fresh and cool. So the damsel sat on demurely, pencil poised above note-book, and did not budge.

But to his misfortune, the Professor's words, unlike his glance, were not specific; and while he waited expectantly, with his eyes fixed upon the static lassie, a dynamic laddie arose in the back row, descended the sloping gangway with thunderous tread, and stalked solemnly out through the open doorway in full view of the spellbound Professor and his momentarily dumbfounded class. And, lo, the departing figure was the figure of that mighty man of valour and hero of a hundred stricken fields—the lion-hearted Jumbo Woods.

CHAPTER XII

FINAL FRAGMENTS

The Bonnie Birds of Belhelvie

ORIGINALLY, guns of all kinds were loaded at the muzzle, the charge of gunpowder being introduced and rammed home before the insertion of the shot or projectile. Breech loading came into use quite early in the development of cannon, although it was not adopted for small-arms until the nineteenth century. Indeed, ancient muzzle-loading fowling-pieces may still be seen occasionally in remote farmhouses, with a receptacle for the ramrod beneath the barrel, and an accompanying powder-horn.

Until the introduction of the modern percussion system, the charge was fired, or "touched off", through a touch-hole by means of a priming of gunpowder. The priming itself was ignited in the early days of firearms by the use of a slow-match, made of cotton soaked in a strong solution of saltpetre, or such-like material (p. 74). Later, in the wheel-lock gun, ignition was brought about by means of a spark, produced by friction between a revolving steel disc, situated at the side of the priming-pan, and a fragment of iron pyrites on which the disc, or "wheel", rested. In the second half of the seventeenth century the wheel-lock was superseded by the flint-lock: in this, the pull of the trigger, instead of rotating a disc, caused a flint to strike sharply against a steel pan-cover, thereby exposing the priming-powder in the uncovered pan to the action of the spark. The flint-lock remained in vogue for about two hundred years and developed into a very efficient weapon, its chief drawback being the delay between the fall of the hammer and the ignition of the charge.

In the year 1800 came the discovery of mercury fulminate by Howard (p. 130). While Howard was carrying out his dangerous experiments in England, an ardent sporting minister in the

north of Scotland was giving equal attention to his favourite recreation of fowling. The Rev. Alexander Forsyth, minister of Belhelvie, a few miles from Aberdeen, was no ordinary man. When he found that his bag was continually suffering through the wary northern birds swerving at the flash and fizzle of his flint-lock priming, his fulminations took a very practical form. He began to experiment with a new system of ignition. Eventually, on July 4th, 1807, he patented a gun-lock for direct ignition of the charge by the flame produced when a small priming of a "detonating powder" (composed chiefly of potassium chlorate) was struck with a hammer. This was the first percussion gun, and it must have bothered the birds of Belhelvie considerably; for the priming no longer flashed and fizzled, and the minister became much quicker on the trigger. Tradition says that Napoleon offered him £20,000 for the patent, which the good man refused. The novel feature of the percussion system, introduced in this way by Forsyth, is that a sudden impact upon a sensitive composition starts an explosive reaction with the production of a hot flame; this, in turn, fires the charge of powder.

How Shot-Gun and Rifle Cartridges Work

The invention of the percussion cap followed a few years later, about 1814. This cap, consisting of a small hollow cylinder, open at one end, was originally made of steel; but copper was soon found to be preferable. The lining of the early caps was mercury fulminate mixed with a little wax or gum. The impact of the gun-hammer upon the base of the cap caused the fulminate to explode and thereby to ignite the charge in the gun-barrel. When Queen Victoria came to the throne, in 1837, the flint-lock was being rapidly superseded by the percussion-lock, and this system of ignition has remained unaltered in principle from early Victorian days for all kinds of firearms. The rifled musket, or rifle, came into general use about 1855: the grooved bore of rifled weapons imparts a spin to the bullet or projectile (p. 147), and thus renders its flight more accurate. Breech-loading rifles were used in the American Civil War, and were generally adopted about 1867.

The old muzzle-loading fusil, musket, or Brown Bess, was not always loaded from a powder-horn. A rudimentary form of cartridge gradually came into use, in which the bullet and gunpowder were wrapped up together in a paper cylinder. When loading his piece, the fusilier or musketeer bit off the end of the paper, poured the powder into the muzzle, and rammed down the bullet and cartridge-paper on the top of the charge with his ramrod. The introduction of the percussion cap, followed by

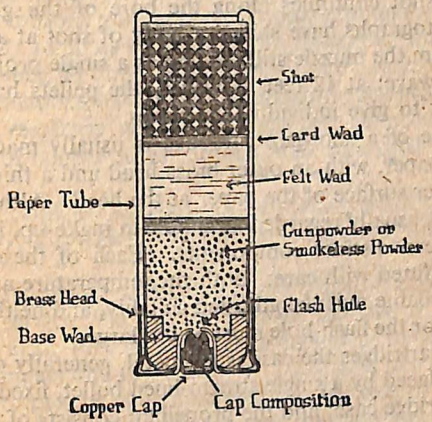


FIG. 10.—A SHOT-GUN CARTRIDGE
(Vertical section)

breech loading, led to the evolution of the cartridge in its modern form for all kinds of small-arms.

An ordinary breech-loading shot-gun cartridge, 2½ inches in length, is shown diagrammatically in vertical section in Fig. 10. The copper percussion cap, having a diameter of about one-fifth of an inch, is situated in the middle of the base; it is enclosed in an inverted brass cap-chamber, with a flash-hole at the top. A thin piece of brass, known as the anvil, fits into the copper cap and rests with its point on the cap composition lying on the

base of the cap. The trigger actuates a mechanism which causes a striker to deliver a heavy blow on the middle of the copper cap: this forces the point of the anvil violently against the sensitive cap composition, and the flame of the resulting detonative reaction passes through the flash-hole and ignites the adjacent charge of gunpowder or smokeless powder grains. The pressure of the explosion gases is exerted upon the central wad of greased felt, and this in turn communicates the propulsive impulse to the charge of shot. The push exerted on the wad and shot continues along the bore of the gun. Quayle spark photographs have shown a body of shot at a distance of 3½ feet from the muzzle still moving as a single projectile with a single air-wave; at 12 feet, however, the pellets had separated sufficiently to give individual air-waves.

The tube of a shot-gun cartridge is usually made of strong cartridge paper, with an outer brass head and a thin iron lining on the inner surface of the paper at the head. Although such a cartridge is usually regarded as simple in make-up, it consists of about sixteen distinct components. Each of these has to be made and fitted with care. Both the temperature and the force of the cap flame must be adjusted suitably, and neither the cap-chamber nor the flash-hole must be too large.

In rifle cartridges the case is all-metal, generally of brass; the shot is replaced by a single stream-lined bullet, fixed in the neck of the cartridge case; and the propellant consists of thin threads of cordite (p. 111). Pistol and revolver cartridges are very similar, but smaller.

The bullet emerging from the muzzle of a rifle may be travelling at some three thousand feet per second, but in spite of such high velocities Philip Quayle found it possible to apply the technique of spark photography to the study of the ballistics of small-arms. This method utilises electric sparks, lasting as little as one or two millionths of a second, for recording silhouettes of objects moving at great speeds. No bullet gives a gas-tight fit in the bore, and the spark silhouettes show that explosion gases leak past the bullet while it is still in the barrel and emerge from the muzzle ahead of it (Plate V). In the same way it has been shown that a bullet fired from a ·30 calibre Springfield rifle is no longer

affected by the propelling gases at so short a distance as 11 inches from the muzzle: formerly it was held that an effective accelerating action persisted through a much greater range.

Points About Percussion Caps

An effective percussion cap must give a hot and sufficiently large flame upon detonation by impact. The common ingredients of cap compositions are mercury fulminate, potassium chlorate, and antimony sulphide (stibnite). The so-called "three-element cap", containing all three ingredients, gives the best results. The following equations have been put forward to represent highly exothermic reactions which are supposed to occur with the production of temperatures between 3500° and 4500°:—

$$Sb_2S_3+3KClO_3=3KCl+Sb_2O_3+3SO_2,$$
$$3Hg(ONC)_2+2KClO_3=2KCl+3Hg+3N_2+6CO_2.$$

Mealed gunpowder and sulphur are sometimes added, as in the British service ·303 cap, to increase the size of the flame. Sometimes also, powdered glass is included to increase the friction of impact and the sensitivity. Attempts have been made to find substitutes for potassium chlorate, because of the corroding action of potassium chloride on the rifle barrel, and for mercury fulminate, because of the deleterious effect of the derived mercury on the brass cartridge-cases. Barium nitrate and lead azide have been tried, but they are less sensitive than the original substances, and lead azide tends to react with the copper cap, as already mentioned (p. 133). Lead styphnate is sometimes used in place of mercury fulminate.

A cap composition must possess the right rate of burning for its specific purpose, and in practice the best composition for a particular kind or form of propellant has to be found by experiment. Cordite, for example, is harder to ignite than gunpowder, and therefore it needs a composition which burns more slowly and produces a longer flame.

The following table gives a few typical cap compositions, and

it may be added that the charge for the first of these is 0·22 to 0·25 grain (0·014 to 0·016 gram):

	For black gunpowder (British service)	*For small-arm ammunition cordite (British service)*	*For small-arm ammunition cordite (German service)*	*Artillery cartridges (two examples)*	
Mercury fulminate	37·5	19	27	15	7
Potassium chlorate	37·5	38	37	45	45
Antimony sulphide	25	43	29	33	30
Glass powder ..	(sometimes to 12·5)	—	6	7	4
Sulphur	—	2·5	—	—	—
Mealed gunpowder	—	2·5	—	—	14
Shellac	—	—	0·6	—	—

SOME TYPICAL CAP COMPOSITIONS

Detonators and their Fuzes

Cap compositions are detonating mixtures applied in a special way in a percussion cap; the effect is produced by a hot flame. Similar mixtures are widely used in small portable metal cases or capsules, known as detonators; but here the effect is usually due to a detonation wave. A copper tube closed at one end is often used as a container for the detonating mixture, and this simple form of detonator may be fired by means of a safety fuze crimped in its open end, or, alternatively, by the use of a detonating fuze; electrical ignition, either by spark or hot wire, may also be used. The detonator originated in Nobel's discovery, in 1864, of the principle of sympathetic detonation (p. 86). For many years mercury fulminate remained the chief constituent of mixtures for detonators; but in 1908 lead azide, although subject to certain disadvantages (p. 133), was introduced as a substitute of superior power and keeping qualities. Tetryl, TNT, and other powerful nitro-explosives have also been used as constituents of detonator mixtures.

A generally accepted series of detonators of standard strengths, denoted by the numbers 1 to 10, has been devised, containing the

following amounts of a filling composed of 80 per cent. of mercury fulminate and 20 per cent. of potassium chlorate:

No.	1	2	3	4	5	6	7	8	9	10
Charge (grams)	0·3	0·4	0·54	0·65	0·8	1·0	1·5	2·0	2·5	3·0

STANDARD DETONATORS

Various references to this series have been made in the foregoing chapters, as for example on p. 96. The less sensitive explosives call for the use of detonators with the higher numbers: thus, Nos. 5 and 6 usually give satisfactory results with nitroglycerine explosives, while the more resistant ammonium nitrate compositions require No. 7.

When other ingredients are used in mixtures for detonators, the power of these so-called "composite" detonators is adjusted to conform to the numbered scale: for example, a detonator containing 0·4 gram of mercury fulminate and 0·4 gram of tetryl corresponds to No. 6.

The use of blasting explosives with detonators has revolutionised the excavation and removal of rock. Before the introduction of explosives this was done by hand, with hammer and chisel, supplemented by "fire-setting", or splitting and flaking the rock by building fires against it and then throwing cold water on to the heated surface. In blasting operations, cartridges of a suitable dynamite or other explosive are solidly tamped in holes drilled in the rock. A detonating cap of the right power is crimped on the end of a fuze and embedded in the last cartridge, and the charge is fired by actuating the fuze.

The Bickford safety fuze, devised originally in 1831 and often used for firing detonators, consists essentially of a train of gunpowder, of fine grain and constant composition, embedded in a flexible and waterproof cable. Various methods are in use for controlling the speed of such fuzes: for example, the rate of burning of the powder may be decreased to about one-twentieth by the addition to it of 10 per cent. of rosin. Detonation fuzes, containing explosives of high brisance, were first introduced in 1904. An electrical fuze, much used in mining work, consists of two fine insulated copper wires which are sealed into the mouth of the detonator tube by means of a mixture of bitumen (asphalt)

and sulphur. The bare ends of the wires rest in a layer of loose detonating composition succeeded by pressed composition at the end of the tube. The fuze wires are connected with long leading wires which may be switched into a low-tension circuit. This method of firing is not only very safe, but it has also the great advantage of permitting a series of charges to be fired simultaneously.

Q.F. and B.L. Cartridges

In the cartridges of shot-guns and rifles only two chemical processes are concerned, namely, (1) the detonation of the cap

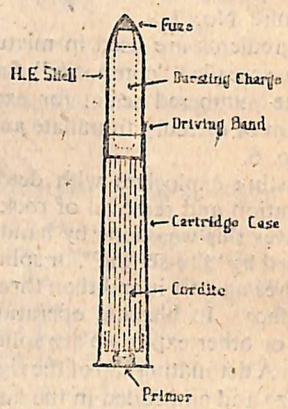


FIG. 11.—A Q.F. CARTRIDGE

composition and (2) the burning of the gunpowder or smokeless powder. In naval and field guns and howitzers another process comes into play, namely (3) the detonation of the bursting charge in the projectile. The cartridges are of two types, known according to the British terminology as "quick-firing" (Q.F.) or "breech-loading" (B.L.) guns. In both types the propellant consists of strands of cordite made up into bundles.

The Q.F. cartridge is essentially an enlarged form of the rifle cartridge, in which a hollow projectile, or shell, replaces the solid bullet (see Fig. 11, which is drawn to a much smaller scale

than Fig. 10). The brass cartridge-case contains the cordite propellant; the primer, or large percussion cap, is screwed into its base; and the projectile is fixed into its neck. Detonation of the cap composition is brought about by the impact of the firing mechanism. Since the ensuing flame would often fail to fire the stout strands of cordite, the primer contains a small charge of gunpowder inserted between the cap composition and the propellant: thus, the flame first fires the powder, and the powder then fires the cordite propellant.

In the larger B.L. guns, the cartridge forms an independent unit of the round, consisting of cordite bundles made up into bags of silk, shalloon, or serge (Plate VI). Small igniter bags of shalloon, containing gunpowder, are stitched on to the end of the cartridge: these serve to communicate the ignition flame from the priming charge to the cordite. The ignition of this type of cartridge is brought about by the use of a brass ignition tube which also forms an independent unit of the round: it contains a charge of fine-grain powder which may be fired either by means of a percussion cap included in the tube or electrically. In B.L. guns the cartridge and the projectile are thus loaded separately. It is evident that the explosives contained in the projectile have to be sufficiently stable to withstand the shock of discharge from the gun.

Shells and their Fuzes

In modern guns the projectile is almost invariably a shell, the chief types being common pointed (C.P.), high explosive (H.E.), armour-piercing (A.P.), shrapnel, and special (gas, smoke, star, and incendiary). These are made of steel, with copper driving bands, which act in conjunction with the rifling of the gun-barrel to impart the necessary spin and thus stability to the projectile when in flight.

The charge in an ordinary H.E. shell is fired on impact by a so-called fuze which screws into the nose of the shell (Fig. 11). Shell fuzes are of many types, and the mechanisms of some of them are very delicate and complex. The percussion direct action (D.A.) fuze operates by means of a metal hammer which impinges violently on a detonating charge when impact occurs. Usually a

gaine of tetryl, or some other suitable "booster", or "exploder" (Plate VII), is interposed between the detonator and the main charge of TNT, amatol, and other high explosives which do not detonate readily. Point (or nose) fuzes give rapid action, but with A.P. shells base fuzes are used. Shrapnel and anti-aircraft shells are fitted with time fuzes: these may be actuated either by compressed trains of gunpowder in adjustable rings (composition type), or by clockwork (mechanical type). Graze fuzes are of a still more delicate type. The assembling of fuzes is one of the numerous specialised operations of a modern munitions factory (Plate VIII).

The sequence of chemical events when a Q.F. gun is fired is thus as follows: [In the gun] (1) explosion of detonation mixture (primer), (2) ignition of gunpowder (primer), (3) ignition of cordite (cartridge) ——→ [At impact of shell] (4) explosion of detonation mixture (fuze), (5) detonation of gaine (fuze and shell), (6) detonation of high explosive (shell). A similar sequence holds for the B.L. gun.

Bombs and Mines

The charges and methods of detonation of bombs dropped from aircraft resemble those in use for shells, but as the bomb is not subjected to the same stresses as a shell the steel container is usually much thinner. The fuzes may be made alive by the removal of a safety pin before the bomb is released, or by the action of the air streams on "arming vanes" during the fall. The maximum speed of such bombs is about 1100 feet per second, or little more than half the muzzle velocity of the shell from a powerful gun. The bombs are usually pear-shaped with a stream-lined tail. *Fragmentation bombs* are very much smaller than *demolition bombs*. Delayed action in bombs may be secured in various ways, notably by a clockwork mechanism, or, in the *magnetic mine*, by the movement of a sensitive needle under the influence of a magnetic field provided by a moving ship. A cruder kind of delayed-action bomb, capricious in its action, has sometimes been made by allowing two fire-producing chemicals to come into contact through the corroding action of one of them upon its

container. The magnetic mine is a special type of submarine mine, the ordinary types of which are essentially large bombs actuated by contact.

Incendiary bombs are not essentially explosive, although they may contain an incidental explosive charge. The main filling is a form of thermite, such as ferric oxide and aluminium powder (used normally for autogenous welding), which gives rise to a highly exothermic reaction when initiated, metallic iron being liberated in an intensely hot molten condition:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

The action is started by a striker in the nose of the bomb; upon impact this fires a detonating composition, which in turn actuates a suitable intermediate chemical reaction (such as that between barium peroxide and magnesium powder) capable of amplifying the heating effect to the temperature required for igniting the thermite. The case of the bomb is made of magnesium or a magnesium-aluminium alloy, and this in turn is thrown into incandescent oxidation. The incendiary effect is produced partly by the molten iron and partly by the burning container: it is due ultimately to the great evolution of heat resulting from the combination of aluminium and magnesium with oxygen.

Grenades

Grenades (French, *grenade* pomegranate—from the shape) are essentially small bombs or shells capable of being thrown by hand or propelled from a rifle. The *Mills grenade* is a small barrel-shaped missile, made of segmented iron; it weighs about 1½ lb. and is easily held in the hand. The main charge is 2½ to 3 oz. of amatol or ammonal. The grenade becomes sensitive when the safety pin is removed. At that stage a lever is held down to the surface of the grenade by the pressure of the hand. When the grenade is thrown, the lever drops off and the grenade becomes alive. A striker actuated by a strong spring falls upon a detonating cap; this in turn ignites a short piece of safety fuze, usually timed to burn for 5 seconds; finally, the fuze fires a detonator and explodes the charge.

A Last Analysis

Modern warfare makes heavy inroads upon the world's supplies of carbohydrates, fats, and coal, in the manufacture of explosives. During the war of 1914-1918 their total manufacture in Great Britain alone exceeded 750,000 tons. The weekly production of cordite rose to 2000 tons, and this single item called for the weekly consumption of 700 tons of cotton from 1060 tons of cotton waste, 374 tons of glycerine from 2700 tons of fat, and 1200 tons of alcohol and ether from 4200 tons of grain. Toluene and other substances were distilled on a vast scale from coal tar, and enormous quantities of pyrites and Chili saltpetre were used in making sulphuric and nitric acids. Still other valuable commodities applied to the same end ranged over the whole chemical gamut from elementary mercury to the complex protein of silk. From the scientific point of view this gigantic burnt-offering to insatiable Mars has no redeeming feature.

Explosives are inseparably linked in the popular mind with the propulsion of missiles, the bursting of bombs and shells, and destructive activities in general. It must not be overlooked, however, that the same agents are widely applied in vital industrial and engineering operations that would be impracticable without their aid. In peace time such activities as quarrying, mining, tunnelling, and the construction of roads and railways utilise a far larger quantity of explosives than is required for military and naval purposes. In 1913, for example, more than 15,000 tons of explosives were used in the mines and quarries of Great Britain alone, and at the present day the total annual consumption for civil purposes runs into hundreds of thousands of tons. Under proper control, explosives have an unrivalled capacity for doing useful work, as demonstrated in such wonderful undertakings as the construction of the Simplon Tunnel and the Panama Canal.

In brief, explosives, like so many other human inventions and discoveries, from fire onwards, are good servants but bad masters.

It is said in Arabian mythology that the greatest of the Djinn was Eblis, who seems to have been the upshot of an efficient explosion, since he was formed out of smokeless fire. His powers were great; but the achievements of Eblis and his numerous

colleagues in the Arabian Nights, as well as those of that indefatigable demon of Michael Scot who "cleft Eildon hills in three", fade into insignificance beside the super-Herculean tasks rendered possible through the use of modern explosives. In a properly ordered human society, explosives, like the products of all other scientific discoveries, would be made to work solely for the benefit of mankind.

Coleridge's last analysis of the strivings of a lifetime, the ephemeral nature of earthly things, and faith in eternity, stands as a masterpiece of concise poetic expression:

> The Knight's bones are dust,
> And his good sword rust;
> His soul is with the saints, I trust.

An equally famous passage from Shakespeare may serve as a farewell to those invisible but highly organised molecules which have formed the subject of this enquiry. At the last, their pent-up energy thrown to the winds, these complex and delicately poised microcosms, built up at the cost of so much material and effort and ingenuity, revert to an intangible chaos of burnt-out gases:

> These our actors,
> As I foretold you, were all spirits, and
> Are melted into air, into thin air.

THE END

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[*Elliott and Fry*

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